

CHEMICAL ABSTRACTS

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1—APPARATUS

C. G. DERICK

An internally heated laboratory vacuum pan. J. F. BREWSTER. *Ind. Eng. Chem.* 15, 139(1923); illus. E. J. C.

Note on dispensing bottle for concentrated alkali solution. W. J. GELDARD. *Ind. Eng. Chem.* 15, 153(1923). E. J. C.

Simple apparatus for comparing the thermal conductivity of metals and very thin specimens of poor conductors. M. S. VAN DUSEN. *J. Optical Soc. Am.* 6, 739-43 (1922).—The method consists in comparing the temp. gradients in two materials placed in series, the rate of flow in each being the same. App. for this investigation is fully described and data are given for contact material including dry boundary, contact water, mineral oil, and various thicknesses of paper and mica, between two horizontal cylinders. The thermal conds. of Zn, Al, Sn, Pb, and Navy brass detd. in this app. check previous values in every case within 5%. E. F. PERKINS

Improvements in measuring apparatus for gases, vapors, liquids and granular substances. F. M. BAYER. *Chem. App.* 9, 78-81, 110-11, 133-5, 144-6, 156-8, 221-3, 231-3(1922).—A review of Ger. patents, with 40 cuts. Cf. C. A. 16, 1683. J. H. M.

Chemical apparatus and technical instruction. O. LIESCHKE. *Chem. App.* 9, 229-31(1922). J. H. MOORE

A new vessel for electrometric titration. W. T. BOVIE. *J. Am. Chem. Soc.* 44, 2892-3(1922).—A vessel of Pyrex glass suitable for class-room use, and cheaper and less complicated than the Clark electrode. D. E. S.

An improved optical lever manometer. E. K. CARYER. *J. Am. Chem. Soc.* 45, 59-63(1923).—The sensitivity of the optical lever manometer of Shrader and Ryder (C. A. 13, 1777) has, by a few changes, been increased to about 0.0001 mm., with an accuracy of about 0.0002 mm. of Hg. DONALD W. MACARDLE

Improved automatic regulator for pressures below atmospheric. W. A. JACOBS AND P. A. COLLINS. *Chem. Met. Eng.* 27, 1129(1922); 1 fig. DONALD W. MACARDLE

Colloid mill and the ultra-filter press. A. W. KENNEY. *Chem. Met. Eng.* 27, 1080-5(1922).—Two types of colloid mill are described: (1) an impact mill in which the charge of liquid and ground solid is "beaten" by a toothed wheel revolving at very high velocities (up to 12,000 r. p. m.) and (2) a friction mill in which the charge is forced axially under pressure between 2 disks rotating rapidly in opposite directions. By the use of these mills it is possible to form colloidal solns. of diverse types of solids (wood, oil shale, phosphate rock, etc.) and various tech. applications are suggested. The use of the mill also has a tendency to improve reaction conditions between 2 liquids or a liquid and a solid. In the ultra-filter press the excess of dispersion medium may be removed from the colloidal soln., forming a paste of the colloid, and yielding a clear filtrate; the operation is continuous. A bibliography is given. D. W. M.

A small high intensity mercury arc in quartz glass. L. J. BUTTOLPH. *J. Optical Soc. Am.* 6, 1066-71(1922).—This illuminator is a self-contained unit furnished to operate on 110 v. either a. c. or d. c. The effective light source has an area of $\frac{1}{4}$ " \times $\frac{1}{4}$ " and is provided with a removable mica filter for absorption of extreme ultra-violet,

an adjustable slit, and a light-tight holder for filters. By use of Corning G555P and G34 glasses λ 5461 may be isolated; or by use of Noviol A and G 585 glasses λ 4359 may be obtained as monochromatic light sources. By use of Wratten filters other lines may be isolated. The instrument has two operating conditions. With enough resistance in series it is a low pressure arc giving only the strongest spectrum lines, and if operated at highest intensity it changes to a high pressure arc giving a continuous spectrum with additional Hg lines.

D. E. SHARP

Regulator circuit. A. T. LARSON. *J. Am. Chem. Soc.* **44**, 2893-4(1922).—Spark-ing at the Hg surface is eliminated by making a feeble current flow through the relay continually, and by connecting the Hg regulator so that it short-circuits the relay.

D. E. SHARP

A high-temperature regulator for use with alternating current. H. S. ROBERTS. *J. Optical Soc. Am.* **6**, 965-77(1922).—R. describes a modification of his high-temp. regulator (*C. A.* **16**, 365) for use with a. c. instead of d. c. The app. is in the main exactly the same as the d. c. app. except that a more satisfactory relay has been developed, and a rectifier placed in galvanometer circuit. The sensitivity is about the same as in the d. c. app., actual tests giving about $\pm 0.1^\circ$ at 1000-1400°.

D. E. SHARP

The pumping of liquids in chemical plants (ROBINSON) 13.

Air filter. C. E. and S. C. DAILEY. U. S. 1,439,151, Dec. 19. Filtering material is held between perforated plates spaced from the top and bottom of a filtering chamber.

Heating water. C. O. BASTIAN and T. G. HAWARD. Brit. 180,710, Dec. 3, 1920. A boiler for providing a supply of hot H₂O at const. temp. below b. p. consists of a water-confg. vessel heated continuously by a burner and having a sheet of non-corrodible metal, such as Ni-Cr alloy, fixed in, upon, or just below, its copper bottom in the region of the flame, and means such as a ball cock for allowing H₂O to flow slowly into the vessel at a fixed predetd. rate. The size of the flame is so fixed that the temp. of the H₂O can never rise above say 150° F. H₂O flows in at such a rate that the vessel is filled in about 20 hrs. Cf. 152,721.

Evaporator for liquids. E. WIRTH-FREY. U. S. 1,437,698, Dec. 5. A closed receptacle for evapg. liquids from which deposition occurs contains concentric annular heating devices which are hollow for passing a heating medium through them; they are provided with external clamp-like scrapers for removing solid deposits from their surface.

Apparatus for emulsifying liquids. E. E. WERNER. U. S. 1,438,733, Dec. 12. An emulsifier disc upon a rotating shaft emulsifies liquids supplied to a tank in which the disc and shaft are mounted.

Means for dissolving chemicals. E. W. THOROLD. Can. 226,901, Dec. 5, 1922. Reissue of Can. pat. 179,676 (*C. A.* **12**, 3).

Chemical and assay balance. D. MCINTOSH. U. S. 1,437,768, Dec. 5. A blower is fixed to the balance case with a tube discharging directly under one of the scale pans, to control oscillations of the balance.

Grates for sintering pans. J. E. GREENAWALT. Can. 225,848-9, Nov. 14, 1922.

Ozone generator. H. B. HARTMAN. Can. 225,949, Nov. 14, 1922.

Apparatus for mixing lime and sugar juice or other liquids. W. MAUSS. U. S. 1,438,843, Dec. 12.

Gas mixing device. G. S. BARROWS. U. S. 1,437,883, Dec. 5. The device is adapted for regulating burner flames.

Reducing valve for gas burners. L. MOMBARUZZO. U. S. 1,437,437, Dec. 5.

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

Pioneer Yale chemists. W. T. READ. *Ind. Eng. Chem.* **15**, 204-6(1923).—Brief biographical sketches, with portraits, of Benjamin Silliman, Sr., Samuel W. Johnson, J. Willard Gibbs and Russell H. Chittenden. E. J. C.

Paul Jannasch. W. STRECKER. *Ber.* **55A**, 194-210(1922). E. J. C.

Edvard Immanuel Hjelt (1855-1921). OSSIAN ASCHAN. *Ber.* **55A**, 163-93 (1922).—An obituary with portrait and bibliography. E. J. C.

Al Rázi as a chemist. JULIUS RUSKA. *Z. angew. Chem.* **35**, 719-21(1922). E. H.

Edward Williams Morley. H. S. BOOTH. *Ind. Eng. Chem.* **15**, 194-5(1923).—Biographical with portrait. E. J. C.

Wilhelm Ostwald. ANON. *Umschau* **26**, 701-3(1922).—A biography, with portrait. E. J. C.

Chemical education and resources of West Virginia. F. E. CLARKE. *Chem. Age* (N. Y.) **30**, 527-30(1922). E. H.

The chemist's education. M. G. KORSUNSKY. *Ind. Eng. Chem.* **15**, 186-90 (1923).—A criticism of existing methods and a suggested solution by one who has been "in intimate contact with the seamy side of the recent period of economic reverse." E. J. C.

Political economy and technology in chemical instruction in the higher schools. P. STAUTZ. *Z. angew. Chem.* **35**, 727-8(1922). E. H.

A lecture experiment demonstrating adsorption. H. G. TANNER. *J. Am. Chem. Soc.* **45**, 437-8(1923). E. J. C.

The advantages of the lecture system of teaching in a technical school. W. R. VRAZEEY. *Eng. Education* **13**, 177-87(1923). E. J. C.

Research bureau laboratory, Standard Steel Car Co. RICHARD RIMBACH. *Chem. Met. Eng.* **28**, 110(1923). E. J. C.

The alchemy of the Arabs. EILHARD WIRDEMANN. *Abhandl. Geschichte Naturwiss. u. Med.* **5**(1922); **Arabic chemistry.** F. J. HOLMYARD. *Nature* **110**, 573-4 (1922).—H. comments on the paper of W. E. J. C.

Chemical formulas. J. H. FRYDLENDER. *Rev. prod. chim.* **25**, 793-6(1922).—A discussion of the various systems of notation at present in use, with a view to obtaining, as far as possible, international uniformity. A. P.-C.

Radion. Proposition of a small unit of mass. M. CENTNERSZWER. *Rec. trav. chim.* **41**, 580(1922).—For convenience in modern "ultrachemistry" C. proposes a new unit: 1 radion = ρ = the mass of one $\mu\mu^3$ of H_2O at $4^\circ = 10^{-24}$ g. On this scale the mass of one H atom = 0.00162 ρ , that of a mol. of O_2 = 0.05 ρ , that of a mol. of sucrose 0.554 ρ , while the mass of colloidal Au particle $2\mu\mu$ in diam. = 200 ρ . E. J. W.

The tables of chemical elements and kinds of atoms issued by the German Atomic Weight Commission. ORTO HAHN. *Naturwissenschaften* **10**, 934-40(1922).—Meyer in a general survey of at. wts. (cf. *C. A.* **17**, 4) limited his discussion to "practical" at. wts. Supplementary to this, a complete table and discussion are given of all elements, including isotopes and at. nos. C. C. DAVIS

Missing elements in the periodic table. F. H. LORING. *Chem. News* **125**, 309-11(1922).—From mathematical relations between the at. nos. of the missing elements (43, 61, 75; 85, 87) it is deduced that either the missing elements do not exist, or if they do exist, they are present in exceedingly minute quantities. A table of elements is arranged consisting of short and long wedges, where all the elements on a given level will be closely allied. JAMES M. BELL

Transference experiments with electrometric derivatives of hydroxylamine. WM. A. NOYES AND J. H. HIBBEN. *J. Am. Chem. Soc.* **45**, 355-9(1923).—Transference expts. with trimethylamine oxide, trimethylhydroxyammonium salts, trimethylmethoxyammonium iodide, trimethylethoxyammonium bromide, trimethyliodomethylammonium hydroxide and trimethylethoxyammonium hydroxide show that in each case a hydroxy, methoxy or ethoxy group remains with the nitrogen as a part of the cation. The attachment of these groups to the nitrogen must be very different from that of the hydroxyl or other atom or group which travels toward the anode during the electrolysis. The resistance offered by the solutions of trimethylamine oxide hydrate and of trimethylethoxyammonium hydroxide seems more consistent with the hypothesis that the hydroxyl ion of these compds. is attached to the nitrogen by a principal valence of such a character that it is only slightly ionized than with that of the unlocalized polar valence assumed by Lewis and Langmuir.

JAMES M. BELL

The crystal structure of silver-palladium and silver-gold alloys. L. W. MCKERNHAN. *Phys. Rev.* **20**, 424-32(1922).—Powder photographs were examd. from thin ribbons of the pure metals and of 7 binary alloys of each series. Both the metals and the alloys have face-centered arrangements of their atoms. The lengths of the edges of the unit cubes are 4.08 Å. U., 4.075 Å. U. and 3.90 Å. U. for Ag, Au and Pd, resp. For both series the edge length is nearly a linear function of the at. % of either component except that *a* is 1% too high for Ag-Au alloys having 30, 40 and 50% Ag. Annealing from 830° to 940° *in vacuo* increases the size of the individual crystals; moderate cold working reduces the size of the individual crystals. From these photographs densities of Ag, Au and Pd are calcd. as 10.49, 19.24 and 11.87, resp.

RALPH W. G. WYCKOFF

The crystal structure of ammonium chloride. R. W. G. WYCKOFF. *Am. J. Sci.* **4**, 469-75(1922).—It is shown that the Laue photographic data obtained from crystals of the low temp. form of NH_4Cl are in agreement with powder data (Bartlett and Langmuir, *C. A.* **15**, 974) in assigning to it a structure contg. one chem. mol. within the unit cube. As a consequence of the disagreement between the symmetry of this uniquely detd. structure and the symmetry as obtained by ordinary crystallographic means, it is pointed out that etch figure data and face development may not be taken as definite indications of the symmetry of the arrangement of the atoms within a crystal.

R. W. G. W.

The crystal structures of potassium chloroplatinite and of potassium ammonium chloropalladites. R. G. DICKINSON. *J. Am. Chem. Soc.* **44**, 2404-11(1922).—The crystal structures of the tetragonal K chloroplatinite and K and NH_4 chloropalladites have been investigated, spectrum and Laue photographs being used. The simplest structure is found which will account for these data. The coordinates of the atoms of the single mol. contained within the unit prism are: K or N at $(0^1/2^1/2)$ $(1/2^0^1/2)$; Pt or Pd at (000); Cl at (uu0) ($\bar{u}u0$) ($u\bar{u}0$) ($\bar{u}\bar{u}0$). The dimensions of this unit prism are:

Crystal.	d_{001} .	d_{100} .
K_2PtCl_4	4.13	6.90
K_2PdCl_4	4.10	7.04
$(\text{NH}_4)_2\text{PdCl}_4$	4.26	7.21

For all of these crystals *u* has been found to be close to 0.23.

R. W. G. W.

The nature of graphite and amorphous carbon. GENSHICHI ASAHARA. *Sci. Papers Inst. Phys. Chem. Research* **1**, 23-9(1922); *Japan. J. Chem.* **1**, 35-41(1922); cf. Debye and Scherrer, *C. A.* **12**, 786.—The essential identity of graphite and amorphous C has been established by the X-ray analysis of 34 different forms of C from different sources. They were ground into fine powder and pressed to layers of about 1 mm. thickness. These were fixed in front of a small window of a wooden box contg. a photographic plate and placed in a lead camera. The interference figure of

the material was recorded on the plate as concentric rings, the plate cutting the mantles of cones of the diffracted rays. Six of these cameras were arranged conically, with the vertex in the source of X-rays facing the X-ray bulb in a shielded box. The interference figures thus obtained constitute an unbroken series, gradually altering from those with 6 comparatively sharp concentric rings of intensity maxima (Type I) to those with an indistinct halo of distributed intensity (Type III). Those whose intensity maxima are not sharply defined but broadened ill-defined bands (Type II) lie between the two extremes. Certain forms of graphite, such as Ceylon and Korean graphites, etc., gave figures with radiant streaks (Type IV), the intensity maxima being common to graphites appearing intact. The streaks may be attributed to the fact that these graphites are only ground along their flat cleavage faces and the incident rays fall chiefly and almost perpendicularly on their cleavage faces. The angles corresponding to the six concentric rings, which the diffracted rays make with the incident rays, are approx. 14° , $18^\circ 50'$, $22^\circ 20'$, $25^\circ 40'$, 31° , and $36^\circ 30'$ resp. The natural and artificial graphites, however finely they may be powd., possess a cryst. structure, as they plainly show sharply defined interference rings. Amorphous C also gives interference figures, but no distinct maxima are observed owing to the distributed intensity. Their estimated maxima are however invariably at about 14° and 23° . Carbons produced by the decomn. of certain gases or vapors, such as CO, C_2H_2 , or CS_2 , or Fe_3C and coal, gave no sign of definite crystalline form, but they gave definite interference figures which establish their cryst. nature. The word "amorphous" must therefore be replaced by "extremely minutely cryst."

K. K.

Identity of amorphous and crystalline silicon. W. MANCHOT. *Z. anorg. allgem. Chem.* **124**, 333-4(1922); cf. *C. A.* **16**, 1521, 3276.—X-ray examn. of the 2 forms of amorphous Si by Debye has shown them to be cryst. and to have the same diamond-like structure as the ordinary form. M.'s assumption that the differences in chem. properties shown by these forms were due solely to greater ratio of surface to mass is thus firmly established. The following additional observation on the chem. behavior of these pseudo-amorphous varieties is appended. When the black variety, obtained by quenching its soln. in metals, is rubbed with PbO_2 , it flames vigorously even in the cold while the yellow-brown variety obtained by action of H_2F_2 on the black variety explodes violently when rubbed with PbO_2 .

A. R. MIDDLETON

The production of carborundum and graphite in electric furnaces. K. P. GRÉGOROVITCH. *Messenger direction générale ind. Métaux russes* No. **1**, 26-36(1921); *Rev. métal.* **19**, 569-71(Abs.)(1922).—G. describes some makeshift contrivances which he had to devise, owing to conditions in Russia. The main difficulty lay in maintaining a const. current, which he did satisfactorily by means of a charcoal rheostat adjusted by hand. The resistance core in the furnace consisted of coke and of old electrodes; instead of pure quartz he used sand (not even absolutely white), and instead of sawdust he used wood shavings, which allowed freer passage of CO and caught fire and ignited the latter when it was evolved in large quantities. Attempts to prep. *graphite* from wood charcoal previously treated with a water-glass soln. were unsuccessful, only a small amt. of graphite being formed exclusively at the surface of the charcoal. The various uses of carborundum are outlined.

A. P.-C.

The structure and chemical activity of copper films, and the color changes accompanying their oxidation. C. N. HINSHELWOOD. *Proc. Roy. Soc. (London)* **102A**, 318-28(1922).—The color changes observed, when bright Cu is exposed to O at low pressures, are due to diffraction and therefore depend on the structure of the film. While the Cu is being activated, by repeated oxidation and reduction, the brilliancy of the colors accompanying oxidation increases with the chem. activity, since the granular film which most effectively scatters light also presents the largest surface to the action

of O. When fresh Cu surfaces are oxidized the colors are faint and their sequence is not const. When Cu which has reached a max. chem. activity is oxidized the color sequence, purple, blue, green, light green, purple, blue, black is reproducible. No diffraction colors appear when the black film is reduced. J. A. ALMQUIST

The crystallography of antimony tribromide. C. B. SLAWSON. *Am. Mineral.* **7**, 173-5(1922).—By subliming this salt and carefully excluding moist air while handling the crystals it was found to crystallize orthorhombic with $a : b : c = 0.7808 : 1 : 1.1645$, and the forms (001), (010), (110), (310), (120), (021), (052), (101), (111) and (221). It is optically negative with extreme double refraction and n much higher than 1.74. Cleavage is unusually good on (010). Crystals kept over CaCl_2 showed superficial alteration to oxybromide. Etch figures suggest bipyramidal symmetry. E. T. WHERRY

Properties of Rochelle salt related to the piezo-electric effect. JOSEPH VALASEK. *Phys. Rev.* **20**, 639-64(1922); cf. *C. A.* **16**, 2632, 4124.—An attempt has been made to obtain information as to the nature of the structure underlying the piezo-elec. effect. In the case of Rochelle salt this effect increases rapidly between -20° and -15° and decreases rapidly between $+20^\circ$ and $+30^\circ$. A study of other phys. properties has been undertaken with the hope of finding some sharp variation in these temp. ranges which would point out a definite relation. The properties studied were, refractive indexes, thermal expansion, sp. rotatory power in aq. solns., elec. cond., electro-optic rotation, and pyro-elec. effect. In view of the fact that none of these properties show changes with temp. which correspond with those of the piezo-elec. effect, it seems probable that the elastic or piezo-optic consts. must change in such a way as to account for the piezo-elec. changes. Rochelle salt seems to form an exception to the Newman principle of symmetry. C. R. PARK

Densities and refractive indexes at 15° of mixtures of water, alcohol and ether. A. SANFOURCHE and A. M. BOUTIN. *Bull. soc. chim.* **31**, 546-51(1922).—This work was undertaken to facilitate the analysis of water, alc. and ether mixts. by phys. methods. The refractive indexes were detd. by means of a Pulfrich refractometer and the densities by means of a Mohr balance. The refractive indexes are given in the tables both in terms of scale readings of the refractometer and n . Two ternary diagrams are given, one for the densities and the other for the refractive indexes at 15° . Pure substances were used throughout the work. W. G. FRANCE

The refractive indices of selenic and selenious acids. H. W. STONE. *J. Am. Chem. Soc.* **45**, 29-36(1923).—The refractive indexes at 20° of from 1% to 99% selenic acid solns. were detd., a max. being found at 97.28%; also those of from 1% to 79% selenious acid solns. BENJAMIN S. NEUHAUSEN

Viscosity and molecular dimensions of hydrogen selenide. C. J. SMITH. *Trans. Faraday Soc.* **1922**, advance proof.—To det. the mean collision area of H_2Se , it is necessary to know the viscosity of the gas and its variation with temp. The gas was prepd. by the action of H_2O on Al_2Se_3 and was shown spectroscopically to be free from H_2S . The viscosity of the gas was compared with that of air by the method of Rankine and Smith (*C. A.* **16**, 668) in which the times required for a Hg pellet to drive equal vols. of the gases through a capillary tube are compared. By this method the viscosity of H_2Se at 20° is 1.68×10^{-4} c. g. s. units. The viscosity of the gas at 0° has been calcd. on the assumption that C/T_B is const. for gases of similar chem. constitution. Here C is Sutherland's const. for the gas and T_B is the b. p. abs. For this gas $C = 365$ and the viscosity of the gas at 0° is calcd. to be 1.55×10^{-4} c. g. s. units. From these results at 2 temps. the mean collision area of the mol. is 0.86×10^{-16} cm.² a result which falls precisely on a curve given by Rankine (*C. A.* **16**, 667) in which the mean collision areas of Kr, HBr and AsH_3 are plotted. This result is consistent with S.'s view that the gaseous mols. HBr, H_2Se and AsH_3 have a central atom which resembles an atom of Kr,

and that the increase in the collision area of the mol. as one passes along the series is to be attributed to the H nuclei which have become attached to the central atom, and that as the H atoms in the mol. increase the distance of each H nucleus from the center of the mol. increases more and more rapidly.

JAMES M. BRILL

Molecular structure and the physical properties of liquids. EDWIN ROSE. *Brit. Assoc. Advancement of Sci., Report 1922*, 40-114.—Beginning with Laplace's theory of capillarity, there is a crit. and highly mathematical review of expts. and theories, including Langmuir's. E. then advances and develops mathematically a theory of mol. attraction, leading to the following law: *Two mols. attract each other with a force that varies inversely as a power of the distance sepg. them, and this power must be higher than the fifth. In all liquids, the result of analyzing the expll. data is to indicate that the mols. attract each other as the eighth power of the distance sepg. them, but Hg is not in good agreement with this law.* Then follow some deductions from this theory, in which are included the views (1) that 94% of the total surface energy of a liquid is located in the surface layer one mol. diam. in thickness, the balance being a greater distance from the surface; (2) that at a distance of 1 mol. diam. from the surface of a liquid, the intrinsic pressure is 8.5% less than the max. value in the interior of the liquids. A long table is given of surface tensions calcd. from latent heats, from compressibility and thermal expansibility, and from d. and thermal expansibility.

JEROME ALEXANDER

Theory of recrystallization. F. KOREF AND H. WOLFF. *Z. Elektrochem.* **28**, 477-8(1922).—A criticism of Alterthum's paper (cf. *C. A.* **16**, 3786). **Reply.** H. ALTERTHUM. *Ibid* 478(1922).

H. JERMAIN CREIGHTON

Graphic gas volume correction. A. W. H. GRIEPE. *Gas Age Record* **51**, 15-7 (1923).—A graphic chart for correcting gas vols. to 60° F. and 30 in. barometer, the curves being based on the formula $V(B + P - A)/T = v(b + P - a)/t$, in which V = corrected vol., B = standard barometer, P = observed gas pressure, T = standard abs. temp., A = aq. vapor tension for standard temp., v = observed vol., b = observed barometer, a = aq. vapor tension for observed temp., t = observed abs. temp. The process of ascertaining the corrected vol. consists in multiplying the observed vol. by a factor corresponding to observed temp. and barometer.

J. L. WILEY

A turbidity standard. H. BECKHOLD AND K. HEBLER. *Kolloid-Z.* **31**, 132-7 (1922).—Standard turbidity is defined as the turbidity of 0.001 M BaSO₄. It is prepd. by mixing 0.002 M hydroxylamine sulfate dissolved in glycerol with a like vol. of 0.002 M BaCl₂ dissolved in glycerol. The av. diam. of the primary particles is 2.5 μ . The standard sol is 0.005 M BaSO₄. It is prepd. by using BaCl₂ and MgSO₄ dissolved in glycerol-isobutyl alc. The standard sol is dild. to the standard turbidity with glycerol contg. 15% isobutyl alc. The standard remains unchanged at least 6 months. The diam. of the particles is not more than 90 $\mu\mu$.

HARRY B. WEISER

The present position of colloidal chemistry. JOSEF REITSCHÖTTER. *Oesterr. Chem.-Ztg.* **25**, 129-31(1922).—A review.

E. J. C.

The field of colloid chemistry. The study of structure. R. ZSIGMONDY. *Z. anorg. Chem.* **35**, 449-51(1922).—In the abstract in *C. A.* **17**, 8, the 5th line, "2 mm. to 40 $\mu\mu$." should read "2 40 $\mu\mu$."

E. J. C.

Capillary chemistry and colloidal chemistry. H. FREUNDLICH. *Kolloid Z.* **31**, 243-6(1922).—An address. A discussion of colloidal substances with reference to surface energy changes and adsorption as capillary phenomena.

A. MUTSCHELLER

Physics of colloidal particles. FELIX EIRENHAFT. *Kolloid Z.* **31**, 239-43(1922).—A lecture reviewing the classification of colloidal systems with definitions and the principal phys. characteristics of each class or type of colloids.

A. MUTSCHELLER

The colloid chemistry of basic chromic solutions. F. L. SEYMOUR-JONES. *Ind. Eng. Chem.* **15**, 75-8(1923).—A review is given on positive and negative hydrous chromic

oxide sols, and of the evidence for the existence of basic chromic salts in soln. A soln. made up to the compn. $\text{Cr}(\text{OH})\text{SO}_4$ passed through ultrafilters unchanged and dialyzed completely through collodion bags.

F. L. SEYMOUR-JONES

The preparation of colloidal solutions of nickel and cobalt hydroxides and some other compounds of these metals. O. F. TOWER AND MARTHA C. COOKE. *J. Phys. Chem.* **26**, 728-35(1922).—Two new methods are given for the prepn. of a colloidal soln. of $\text{Ni}(\text{OH})_2$. A *N* soln. of $\text{NiC}_2\text{H}_4\text{O}_6$ treated with NaOH or KOH soln. forms a green transparent gel. Upon standing several days $\text{NiC}_2\text{H}_4\text{O}_6$ seps. With 0.2 *N* soln. no gel forms but with the ultramicroscope the soln. is shown to be colloidal. After dialysis the soln. contained 3.2 g. $\text{Ni}(\text{OH})_2$ per l. Solns. of Co salts give quite different results owing to oxidation. A gel of $\text{CoC}_2\text{H}_4\text{O}_6$ sometimes forms. Colloidal $\text{Ni}(\text{OH})_2$ is better formed by mixing 0.1 *N* soln. of NiCl_2 and KOH . The ppt. is washed by decantation until, upon standing, it becomes colloidal. This soln. is opalescent, exhibits the Tyndall effect and shows particles under the ultramicroscope. Upon dialysis $\text{Ni}(\text{OH})_2$ ppts. The colloid drifts toward the negative pole upon electrolysis. Colloidal $\text{Ni}(\text{OH})_2$ from the tartrate is more stable than that from the chloride. Glycerol does not hold $\text{Ni}(\text{OH})_2$ in soln. as it does the hydroxides of Co and other metals. A glycerol soln. of $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$ forms a gel with a soln. of alc. KOH .

D. T. EWING

Coagulation of manganese peroxide sol by different electrolytes. PHANT BHOSAN GANGULY AND N. R. DHAR. *J. Phys. Chem.* **26**, 701-14(1922).—A study of the application of the Schulze-Hardy law to the coagulation of MnO_2 sol by 31 different solns. MnO_2 sol was prepd. by the reduction of KMnO_4 with MnSO_4 . Gelatin was used as a stabilizer. Colloidal solns. were treated with each of the 31 solns. and the time for coagulation noted. The coagulative power of each of the solns. was detd. by finding the min. vol. of soln. which would ppt. the sol in 2 hrs. Three different concns. of the sol were studied. The coagulative powers of the different electrolytes on MnO_2 sol show that the Schulze-Hardy law is only partially applicable to this sol. The coagulative power is influenced by the kind of anion, time allowed for coagulation and the concn. of the colloidal soln.

D. T. EWING

Disperse systems in gases. W. E. GIBBS. *Brit. Assoc. Advancement of Sci.*, 4th Report, 1922, 122-85.—This excellent paper treats of mists, clouds, dusts, fumes, smokes, etc., which, as is the case with all colloids, may be formed by condensation or by disintegration methods, which are briefly considered. The properties of these gas-solid and gas-liquid dispersions are then considered as follows: (1) mech. properties (concn., motion of particles, degree of dispersion); (2) optical properties (absorption, reflection, refraction and diffraction of light by the system); (3) thermal properties (absorption and radiation of heat); (4) elec. properties (elec. charges of the particles and their behavior in an elec. field); (5) chem. properties (increased chem. activity consequent upon dispersion). The applications of these principles are considered under (1) recovery of valuable or noxious liquid or solid particles from smokes and mists issuing from smelters, acid concentrators, cement kilns, etc.; (2) prevention of explosions in coal mines, flour mills, etc.; (3) cleaning factory air from poisonous or irritant dusts; (4) prep. finely divided substances, e. g., C black, milk powder; (5) explaining meteorological phenomena; (6) gas clouds and smoke screens in warfare.

J. A.

Cataphoresis-motion of colloidal particles in an electric field. E. F. BURTON. *Brit. Assoc. Advancement of Sci.*, 4th Report, 1922, 23-33.—A general discussion, including cationic and anionic solns.; theory of cataphoresis; detn. of mobility of particles (including tabular results of many experimenters on suspensions, suspensoids, emulsions and electrolytic ions); special uses; electro-kinetic effect of added electrolytes.

JEROME ALEXANDER

Colloidal systems in solid crystalline media. CECIL H. DESCH. *Brit. Assoc.*

Advancement of Sci., 4th Report, 1922, 33-40.—The first part reviews some of our present knowledge on the colloidal dispersion of some of the constituents of *steel and alloys*, and even the *iso-colloidism of pure metals*. Since "the dimensions of the grains are considerably above the limits which are usually assigned to the colloidal state, it is unlikely that any advantage would be gained by including this aspect of the structure of metals under the heading of colloid chemistry." [This is erroneous, because the effects of subdivision transcend the limits mentioned. Besides, visible grains, metals and alloys contain in addition truly colloidal particles. J. A.] A brief very incomplete section on the "*Coloring Matters in Crystalline Minerals*," is also included.

JEROME ALEXANDER

Absorption of fogs appearing in chemical reactions. H. REMY. *Z. Elektrochem.* 28, 467-9(1922).—The fogs appearing in chem. reactions (*e. g.*, SO_4 , NH_4Cl) have been studied. These are divided into two classes: (1) moist fogs, and (2) dry fogs (colloidal dust). Fogs of the 1st class consist of visible particles about 10^{-4} cm. in diam., and are best absorbed by H_2O ; those of the 2nd class consist of almost invisible particles about 10^{-8} cm. in diam., and are best absorbed by concd. salt solns. The latter form visible fogs with moisture.

H. JERMAIN CREIGHTON

Adsorption measurements. H. v. EULER. *Z. Elektrochem.* 28, 446-9(1922); cf. *C. A.* 16, 1351.—The adsorption of Ag by Au and Ag foil (instead of by the metal powder previously employed) from aq. solns. of AgNO_3 of different concns. has been studied. In all of the expts. 5 cc. of AgNO_3 soln. were employed. The area of the Au foil was 5.296 dcm.² and that of the Ag foil 3.111 and 6.238 dcm.². The foil was rolled in such a way that the whole surface was free. With the Au foil the adsorption curve is linear at low Ag concns., then bends and approaches asymptotically a limiting value corresponding to a sorption of 5.5 mg. Ag per m.² of metal surface. The results obtained with the 2 pieces of Ag foil lie on the same adsorption curve. This curve rises more steeply and lies above that obtained with the Au foil. It also approaches asymptotically a limiting value corresponding to a sorption of 8.5 to 9.0 mg. Ag per m.² of metal surface. Within the limits of exptl. error the sorption of Ag is independent of the temp., and also of the solvent as indicated by the results of expts. carried out with AgNO_3 dissolved in 96% alc.

H. JERMAIN CREIGHTON

Gas adsorption on ultramicroscopic particles. M. KÖNIG. *Z. Physik* 11, 253-60 (1922).—By the exptl. method of Radel and the Stokes-Cunningham formula (*C. A.* 14, 464) values for the radius of small particles of Hg were obtained. The elementary charge carried on these particles was measured by their rate of fall in an electrostatic field. This was a function of the radius of the particle and also of the gas in which the particle was falling. At a certain limiting value of radius the value of the elementary charge became const. and this limiting radius depended on the gas. For an easily condensed gas such as CO_2 the value was 2.1×10^{-4} cm. while for air it was 1.2×10^{-5} cm. This is explained on the ground that CO_2 is more easily adsorbed than air and for particles too small the sp. surface is so great that the adsorbed layer retards the movement of the particle, causing its charge to seem small. Air, which is less adsorbed, can stand a higher degree of dispersion (smaller limiting value of radius) without affecting the results. These effects cannot be explained on the basis of a layer of adsorbed gas only one or at most 2 mols. thick as postulated by Langmuir. To have any effect on the thickness of a particle whose radius is 10^{-5} cm. the layer must be many mols. thick.

A. E. STEARN

Theory of electro-endosmosis and ionic double layer based on experiments with carbon filters. L. MICHAELIS. *Z. Elektrochem.* 28, 453-5(1922); cf. *C. A.* 14, 885, 1776, 2574.—The theory of the origin of the elec. double layer by the unequal adsorption of ions is briefly discussed, and the adsorption affinities of different kinds of C are de-

scribed. The adsorption of surface-active nonelectrolytes is practically the same for all kinds of C. On the other hand, different kinds of C behave quite differently with electrolytes. Thus, blood charcoal adsorbs certain anions and cations almost equally well; sugar C and benzoic acid charcoal adsorb ions to a much smaller extent. These last-named varieties of C adsorb cations (methylene blue) to a measurable extent, but they do not adsorb even traces of anions (eosin, picric acid). In view of the work of Gyemant (cf. *C. A.* 15, 1840) and others on electro-endosmosis and ion adsorption, this behavior is to be expected: blood C, as an ampholyte, combines with both anions and cations; sugar C, as an "acidoid," combines only with cations. H. J. C.

Solubility of liquids in liquids. The partition of the lower acids, particularly formic, between water and various organic solvents. N. E. GORDON AND E. E. REID. *J. Phys. Chem.* 26, 773-89(1922).—HCOOH has been partitioned at 25° between H₂O and cottonseed oil, xylene, CCl₄, CS₂, CHBr₃, kerosene, C₆H₆ and C₇H₈. CH₃COOH has been partitioned between H₂O and cottonseed oil and kerosene; propionic and butyric acids between H₂O and cottonseed oil. The solubilities of the 4 acids in the above solvents have been measured and *vice versa* so far as possible. Twelve tables of data are given and the results are discussed in detail. D. T. EWING

Variations of the solubility of a compound through the presence of other compounds.

I. Water-phenol-diphenols. P. LEONE AND E. ANGELSCU. *Gazz. chim. ital.* 52, II, 61-74(1922).—Numerous cases of increase of soly. of a compd. in a solvent by the addn. of another compd. are known and some are reviewed here. A 3rd compd. can influence the reciprocal soly. of 2 liquids and consequently change the crit. temp. L. and A. have studied the reciprocal variation of soly. in the system H₂O-PhOH on the addn. of resorcinol, hydroquinone and pyrocatechol. H₂O and PhOH form 2 liquid layers and have a high crit. temp. (66.6°). The presence of a diphenol causes a marked increase in the reciprocal soly. and a large lowering of the crit. temp. By adding a diphenol at const. temp. to a H₂O-PhOH mixt., sepd. in liquid layers, the comps. of the 2 layers tend to approach each other and at a certain concn. become equal. To establish the concns. of equil. between the 2 liquid phases L. and A. detd. the soly. isotherms at 0° and 10° and then the minimal temp. at which the various ternary mixts. form a single liquid phase. The isotherms were constructed by detg. separately the constitution of the 2 layers in the presence of an increasing quantity of diphenol. A weighed amt. of H₂O in a bath at 0° or 10° was treated with PhOH drop by drop from a Beckmann pipet until it became turbid. The loss in wt. of the pipet minus the drop that causes the turbidity is the amt. of PhOH sol. under the conditions. Resorcinol was then added and the addn. of PhOH repeated to the same point. This was repeated with increasing amts. of resorcinol until 15.52 g. had been added per 100 g. H₂O. The data are given in tables and curves and the conclusions are largely numerical. The results showed that the increase in soly. of PhOH in H₂O does not increase proportionally to the amt. of resorcinol but much more rapidly. It was also found that hydroquinone acts similarly but increases the soly. of PhOH in H₂O less than resorcinol. The min. concn. of hydroquinone above which 2 liquid layers no longer occur is 11.50% at 0° and 10.07% at 10°. With pyrocatechol 2 liquid layers no longer occur above 8.97% at 0° and 8.11% at 10°.

II. Water-epichlorhydrin-acetic acid. P. LEONE AND M. BENELLI. *Ibid* 75-86.—Epichlorhydrin and H₂O are reciprocally little sol. and after being shaken together form 2 layers: the lower of epichlorhydrin satd. with H₂O; the upper H₂O satd. with epichlorhydrin. The reciprocal soly. of the compds. increases with increase of the temp. The crit. temp. of the soln. lying above 80° could not be attained because epichlorhydrin begins to act with H₂O. L. and B. studied the influence of AcOH on the soly. of the 2 liquids at various temps. AcOH is miscible in all proportions with both liquids and increases the reciprocal soly. and thus lowers the crit. temp. In this ternary system

which contains a single pair of components capable of giving 2 liquid phases the conditions of equil. of these 2 phases was studied between 0° and 80° . Three kinds of detns. were made: (1) reciprocal soly. of H_2O -epichlorhydrin was detd. at various temps.; (2) the displacement of the temp. of satn. in the presence of AcOH was detd.; (3) from these data the isotherm was constructed. (1) was detd. by a method similar to that used for PhOH above. The mixts. were warmed slowly until they became limpid and this temp. was the temp. of satn. The data and graphs cannot be briefly abstracted.

E. J. WITZEMANN

A problem in viscosity: The thickness of liquid films formed on solid surfaces under dynamic conditions. RESEARCH STAFF OF THE GENERAL ELEC. CO., LONDON. (Work conducted by F. S. GOUCHER AND H. WARD.) *Phil. Mag.* **44**, 1002-14 (1922).—The detn. of the thickness of the liquid layer coating a solid body drawn out of a liquid is discussed theoretically and practically. It is shown that if the solid is a flat slab of infinite width, the forces detg. the thickness are those of gravity (g) and viscosity (η) and the relation between thickness (l), density (ρ), and the velocity of drawing v_0 is: $l^2 = 2v_0\eta/\rho g$. If the solid is a fine wire of radius r , surface tension is dominant and gravity negligible. If γ is the surface tension, the relation must be of the form: $l/r = f(\eta\rho/\gamma)$. It is found empirically that $f(\eta\rho/\gamma)$ is of the form: $4.8 \eta\rho/\gamma$ in c. g. s. units. These results apply to suspensions if, (1) the diam. of the suspended particles is not greater than l , (2) if the effect of the particles in increasing η is taken into account. There is no evidence of any special cohesion between solids and liquids wetted by them other than that which prevents slipping at the interface.

S. C. L.

The viscosity of liquids and its theoretical interpretation. LEON BRILLOUIN. *J. phys. radium* [6] **3**, 326-40 (1922).—The classical kinetic theory is specially adapted for the study of the properties of a gas in which collisions are rare, but it is of less use when dealing with liquids and solids where the mols. are continually in collision, and where the transfer of matter in the process is ordinarily insignificant. When a mol. strikes, all of the mols. in the vicinity are shaken and an *elastic wave* is formed which is propagated through the medium. To est. the thermal agitation in a liquid or solid, it is necessary to analyze the movement of the elastic wave, the energy and free path of the wave, which are functions of the frequency and temp., being stated. The hypothesis furnishes an explanation of the sp. heat, thermal expansion and the equation of state of solids. The theory of black body radiation bears many points of similarity to this one, but with rather important modifications entailed by the granular structure of matter. The conception of a mean free path in an elastic wave makes it possible to calc. the heat cond. Employing it to calc. the viscosity, B. finds a *negative* viscosity coeff., i. e. the wave of thermal agitation has the effect of diminishing the inherent viscosity of the body. This accords with the fact that at const. vol., the viscosity of a solid or liquid diminishes as the temp. is raised. The *initial viscosity*, which is so great at low temps., is explained by the assumption of an inherent viscosity in all solids and liquids which is progressively counteracted by the influence of thermal agitation as the temp. is raised. This initial viscosity is due to collisions between mols. of layers of slightly different translational velocity. The collisions bring about the emission of elastic waves and consequently the dissipation of energy. The *initial viscosity* should be independent of the temp., provided that the vol. is kept const. The total viscosity is the sum of the initial viscosity and the viscosity due to the thermal elastic wave. Formulas are given which will be deduced in a later paper. The exptl. data at hand shows a general concordance with the theory advanced.

EUGENE C. BINGHAM

Molecular viscosity. F. M. LIDSTONE. *Nature* **110**, 733-4 (1922).—A suggestion that measured viscosity may be composed of two factors, (a) mol. friction or deformation, and (b) gyro-viscosity. As ordinarily conceived the factor (b) is overlooked. It is that

component caused by gyroscopic resistance offered by mol. orbits, after the fashion of twin stars, having components normal to the line of flow. It is suggested that a measure of factor (b) may be obtained by the correct resolution of the forces which go to produce the so-called Couette correction for flow through capillary tube. A. E. STEARN

Constitution of aqueous solutions of thallium salts. C. DRUCKER. *Z. Elektrochem.* 28, 463-7 (1922).—From measurements of the lowering of the f. p. and the concn. tensions of solns. of TlNO_3 , it has been shown that solns. of this salt contain appreciable quantities of Tl_2^{++} -ions. In quant. agreement with independent calcns. from cond. data Ostwald's diln. law is found valid, thus again proving the validity of the law for solns. of ordinary diln. in which "chem. complications" occur. The data obtained for the equil., $2\text{Tl}^+ \rightleftharpoons \text{Tl}_2^{++}$, have been used to recalc. the data previously found with Tl_2SO_4 . Thus, it has been shown that the mobility of the TlSO_4^- ion is normal. In conclusion, the bearing of the results on the question of complete dissocn. of strong electrolytes and on the Ghosh hypothesis is discussed. H. JERMAIN CREIGHTON

Positive and negative valences. WM. A. NOYES. *Rec. trav. chim.* 41, 557-60 (1922).—After a brief historical review of this subject N. describes recent results of Wilson on the cond. of HClO in which it was found that the ionisation of HClO is very low and that it is due almost entirely to H^+ and ClO^- ions while very few OH^- and Cl^+ ions are present. Moreover, although HClO exists in the mol. form a current of air at 25° carries away Cl_2O , which is most readily explained by assuming that HClO undergoes amphoteric dissociation, giving H^+ , ClO^- , HO^- and Cl^+ , of which 2 unite to give H_2O and the others Cl_2O . These results do not agree well with the so-called octet theory of Lewis-Langmuir. They furnish a ready explanation of the action of NaOCl on Me_2CO . In nitration HNO_3 appears to sep. into NO_2^+ and OH^- while sulfonation takes place similarly. Chiles in the same lab. has obtained diazodiethyl glutarate (A) in an optically active form which can be explained if one N is + and the other —, which again is not consistent with the assumption that the union between the 2 N atoms is non-polar. Agreement with the L.-L. theory is better in terms of Angelo-Angeli's formula $\text{R}_2\text{C} \rightleftharpoons \text{N}:\text{N}$ for A. E. J. WITZEMANN

Degree of ionization of ethyl alcohol. I. From measurements of conductivity. P. S. DANNER and J. H. HILDEBRAND. *J. Am. Chem. Soc.* 44, 2824-31 (1922).—Methods of purification of EtOH are given. A sample having a sp. cond. of 1.35×10^{-9} ohms has been prepd. The const. is given as 2.89×10^{-16} for the dissociation $\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{O}^- + \text{H}^+$. II. From measurements of electromotive force. P. S. DANNER. *Ibid* 2832-41.—The const. for the dissociation by this method is 7.28×10^{-20} which is considered a better value than that obtained from cond. measurements. A table of activity coeffs. for HCl in EtOH is given, covering a concn. range from 0.0088 to 0.3 N. C. R. PARK

Direct and indirect ester formation on water-poor and water-rich glycerol. ANTON KALAN. *Rec. trav. chim.* 41, 592-600 (1922).—Owing to the great importance of glycerol esters in nature it was desired to det. the velocity of esterification of organic acids in the presence and absence of mineral acid catalysts. These expts. were made with BaOH since its esterification in EtOH was fully studied (*C. A.* 6, 2872). Pure glycerol was treated with milk of lime to remove acids, filtered, concd. *in vacuo* and fractionated *in vacuo*. The fraction used (b_p 175° , d_4^{25} 1.258) was nearly free from acid. Comparative detns. with HCl -contg. glycerol poor in H_2O and rich in H_2O showed that the addition of H_2O causes a marked diminution in the velocity of esterification. A comparison of the results obtained by G. in EtOH shows that the retarding action of the H_2O on the catalytic influence of HCl in dry glycerol is less than in EtOH . The opposite was expected because glycerol contains 2 CH_2OH groups. This result is also discussed in relation to the data of Michael and Wolgast (*C. A.* 3, 2952) and Goldschmidt

and Thiesen (*C. A.* 7, 1651). Solns. of BzOH in abs. glycerol were heated in sealed Jena tubes in boiling H₂O or PhNH₃. After heating the tubes were cooled in water, opened, washed down with a few cc. EtOH (to prevent pptn. of Ba(OBz)₂) and titrated with Ba(OH)₂ soln. The results showed that under these conditions BzOH in a large excess of glycerol is esterified in accordance with the bimol. law just as is CCl₃CO₂H in EtOH (Goldschmidt, *Ber.* 29, 2208(1896)). On changing from 100° to 182° the velocity of esterification is increased about 250 times or about 2.0 times for each 10° (cf. M. and W. above also).

E. J. WITZEMANN

Studies in acidolysis. I. The equilibrium between acetic acid, trichloroacetic acid, and their ethyl esters. II. The equilibrium between acetic acid, trichloroacetic acid and their methyl esters. J. J. SUDBOROUGH and D. D. KARVE. *J. Indian Inst. Sci.* 5, 1-21(1922).—The method for detg. the free acids, CCl₃CO₂Et and AcOEt in mixts. of the acids and esters was: (1) Titration with standard NH₄OH using Me red, rosolic acid or litmus as indicator gave the amt. of free acids. (2) Titration with standard NaOH or Ba(OH)₂ (using phenolphthalein) and subtracting the free acid obtained in (1) gave the amt. of standard alkali required to hydrolyze the CCl₃CO₂Et. (3) Subtracting from the total amt. of alkali required to complete neutralization and sapon. the amt. of alkali required in (2) gave the amt. of standard alkali needed to saponify the AcOEt. Sapon. with NaOH was usually completed in 12 hrs. The equil. const. for AcOEt + CCl₃CO₂H \rightleftharpoons AcOH + CCl₃CO₂Et varied between 0.98 and 1.08 with an av. of 1.02. For the corresponding Me ester the equil. const. varied between 0.98 and 1.00. Since these const. are practically unity, the affinities of ethoxy or methoxy for Ac and trichloroacetyl groups are practically identical. That acidolysis for Me esters was much slower than for Et esters was shown by calcn. of the value for k/V from the equation, $k/V = (1/2At)\ln[A/(A - 2x)]$. This equation was deduced for the particular case in which A is the initial concn. of AcOEt and of CCl₃CO₂H in mols. per 1000 g. of mixt. and the initial concn. of AcOH and CCl₃CO₂Et is nil, the velocity const. $k_1 = k_2$, x is the no. of mols. in 1000 g. of mixt. transformed in the time t expressed in hrs. and V is the vol. of 1000 g. of the mixt. The formation of intermediate additive compds. in acidolysis analogous to those found in esterification, hydrolysis of esters, and alcoholysis has not been shown.

H. M. McLAUGHLIN

Action of neutral salts on the rearrangement of acetochloroanilide to *p*-chloroacetanilide, as a function of the activity of hydrogen ions. GÖSTA ÅKERLÖF. *Medd. Vetenskapsakad. Nobelinst.* 6, No. 2, 15 pp.(1922); cf. *C. A.* 15, 3417.—Continuing the studies of neutral salt action Å. has employed the data of Rivett (*C. A.* 8, 287) on the rearrangement, acetochloroanilide \rightarrow *p*-chloroacetanilide. The effect of the neutral salt (a chloride) is found from the expression $(K - K_0)/C$, where K is the reaction velocity const. at the concn. (normality) C , and K_0 is the reaction velocity const. in the absence of the salt. In all cases the titration value of the acid HCl is const. The effect of the salts is of the same order of magnitude, and for salts of each valence no. the lower at. wts. have the greatest effect. Thus LiCl has the greatest effect of the univalent chlorides, and MgCl₂ of the bivalent chlorides. The velocity of the reaction at any given temp. and concn. is influenced by the activity of H ions and not by any direct effect of the neutral salt. The relation can be expressed by the formula, $\log(K/K_0) = (D/1 + \sqrt{C}) \log(\alpha/\alpha_0)$, where K is the reaction velocity const., α is the activity of H ions as found by e. m. f. measurements, C is the salt concn. and D is a const. (approx. 0.65).

JAMES M. BELL

Catalytic activity of copper. O. W. BROWN and C. O. HENKE. *J. Phys. Chem.* 26, 715-27(1922).—The reduction of $C_6H_5NO_2$ to $C_6H_5NH_2$ by H in the presence of Cu catalysts has been studied. The catalysts were prepd. by reducing with H the oxide obtained by igniting Cu(NO₃)₂ and from the oxide derived from the action of NaOH on Cu(NO₃)₂.

The latter was the more efficient. 260° was the best temp. for reducing $C_6H_5NO_2$. Cu on asbestos reduced $C_6H_5NO_2$ faster than Cu alone. The activity of thick deposits of Cu on asbestos decreased with high rates of flow of $C_6H_5NO_2$. Cu on pumice was not as efficient as Cu on asbestos. The life of the Cu catalyst was prolonged by the presence of small amt. of Fe.

D. T. EWING

A case of catalysis that could be calculated in advance. E. ABEL. *Rec. trav. chim.* 41, 610-2(1922).—(In German.) In connection with other work the velocity of reduction of IO_4^- to IO_3^- by I^- was detd. E. Müller also found this reaction to be quant. within certain H-ion concns. and convenient for the detn. of IO_4^- with AsO_3^- . The results as obtained in an acetate-AcOH soln. will be described in detail elsewhere; they in general showed that under the conditions used there is a catalysis of the reaction $IO_4^- + AsO_3^- \longrightarrow IO_3^- + AsO_3^-$ by I^- . In this case the velocity of reaction of the uncatalyzed reaction (direct), the catalyzing reaction and the catalyzed reaction could all be detd. separately. This is a rare if not previously unknown case. The results showed that there is a typical catalysis in which the catalyst accelerates a reaction of measurable velocity and that the amt. of this acceleration can be predicted. E. J. W.

The action of boric acid on mannitol in alkaline solution. RENE DUBRISAY. *Compt. rend.* 175, 762-4(1922); cf. C. A. 12, 1355; 16, 2247.—D. has followed the course of the reaction between H_3BO_3 in alk. soln. by measuring (1) the temp. of miscibility with phenol, (2) the optical activity, and (3) the surface tension by the drop wt. method. The reaction is incomplete. The results apparently indicate the existence of at least 2 distinct compds. of mannitol with H_3BO_3 and NaOH, that richer in H_3BO_3 having the greater optical activity.

L. T. FAIRHALL

The degree of molecular polymerization of substances at the critical point. J. A. MÜLLER. *Compt. rend.* 175, 760-1(1922).—M. has calcd. the mean degree of polymerization (\bar{n}) of a number of substances from their crit. data and has shown that at the crit. point all these substances, save He, contain polymerized mols. The value of \bar{n} for the liquid hydrocarbons and their monohalogen derivs. varies between 1.39 and 1.45; for certain esters it varies from 1.45 to 1.48, while for the alcs. it has a somewhat higher value. The nitriles, as well as AcOH and H_2O , have a value for \bar{n} of about 2. There is but little difference in the degree of polymerization of isomers.

L. T. FAIRHALL

Several necessary relations between the physical properties of isomeric organic compounds. ALFONS KLEMENC. *Rec. trav. chim.* 41, 601-9(1922).—van't Hoff showed that there is a relation between polymorphic compds. that become identical in soln. or in the vapor state: $\log P_{II}/P_I = \int_{T_1}^{T_2} (L_{II} - L_I)/RT^2 \cdot dT$, in which $L_{II} - L_I$ is the difference in the heats of soln., P_{II} and P_I are the satn. concns. of the 2 forms at the temp. T , and P is the temp. of the transformation point. The equation does not apply to isomeric substances that are not identical under these conditions and exceptions have also been reported. The equation for those compds. which do not give identical solns. is derived in this paper as follows: $\log (P_{II}/P_I) = (L_I - L_{II})/RT$. According to this 2 isomeric compds. are to be considered as polymorphic compds. having a very high transformation temp., but K. is not disposed to insist upon this since there is apparently a difference in the behavior of the sp. heat. In the case of S the difference in the sp. heat of the 2 modifications varies directly with the abs. temp., while with isomeric compds. the change is inversely proportional to the abs. temp. The equations could not be satisfactorily tested owing to the lack of suitable data. The other equations developed in this paper are briefly tested with soly., vapor tension and sp. heat data of isomeric org. compds. In general it is concluded that surprisingly simple relations appear to exist between these phys. properties of isomeric org. compds. E. J. WITZEMANN

Graphical representation of binary systems. E. TRASENSTHR. *Rev. métal.* 19,

533-8(Abs.)(1922).—A general discussion of the characteristics of temp.-pressure, temp.-concn., and cal.-concn. diagrams of binary systems. A. P.-C.

Heat temperature curves of metals. JOS. F. SHADGEN. *Iron Age* **110**, 218-22 (1922).—A republication, with some discussion, of the results of Wüst, Meuthen and Durrer (*C. A.* **14**, 1241) reduced to English units. W. P. WHITE

Solidification of the system $\text{MgCl}_2\text{-KCl-BaCl}_2$. J. VALENTIN. *Compt. rend.* **175**, 1061-3(1922).—Diagrams for this system are obtained by the methods of thermal analysis. J. A. ALMQUIST

Micro-molecular weight determinations with melting point apparatus. II. Manipulation with extremely small quantities. KARL RAST. *Ber.* **55B**, 3727-8(1922).—App. and procedure are described for the extension of the method of mol. wt. detn. by the lowering of m. p. of camphor (*C. A.* **16**, 2060) to quantities as small as 0.2 mg. Agreement between calcd. and observed values of known compds. is strikingly close.

BENJAMIN S. NEUBAUSEN

The heat of formation of aluminium nitride. FR. FICHTER AND ERNST JENNY. *Helvetica Chim. Acta* **5**, 448-54(1922).—The AlN was made into slender pastils with 50% benzoic acid and burned in a calorimetric bomb in O at 20 atm. The heat of combustion was 3150 cal. per g.; extreme discrepancy was about 3%, with good agreement with other work. The resulting mol. heat of formation is 62 kilocalories, against 190 (Berthelot) for $\frac{1}{2}\text{Al}_2\text{O}_3$. W. P. WHITE

Specific heat at low temperatures. FRANZ SIMON. *Ann. Physik* **68**, 241-80 (1922).—The app. used by Nernst in his work on sp. heats at low temps. (cf. *C. A.* **4**, 2397) has been modified by enlarging it and by increasing the ratio of the sp. heat of the charge to that of the empty calorimeter. The processes of sealing and evacuating the calorimeter and reading the temps. and pressures are minutely described. In the following abstract of the 6 pages of data given, N indicates the no. of observations made in covering the range between the abs. temps. indicated by the next 2 nos. and C_p indicates the quotient found by dividing the mol. heat by the no. of atoms in the mol. Two values will be given, that corresponding to the lowest temp. and that corresponding to the highest temp. "*Lindemannglas*," coarsely powd., $(10\text{Li}_2\text{BO}_7 + 2\text{BeO} + 3\text{B}_2\text{O}_3)$: N 12, T 24.3-114.8°, C_p 0.110-1.198; *crystalbite*, fine powder, (SiO_2) : N 14, T 28.6-116.6°, C_p 0.208-1.560; "*Quartzglas*," coarse powder: N 17, T 18.9-287.6°, C_p 0.107-3.454; *Hg*, distd. *in vacuo*: N 15, T 18.7-231.8°, C_p 2.252-6.863; NH_4Cl , very pure, finely powd. N 52, T 20.1-290.8°, C_p 0.0596-3.391; *CaI*, melted *in vacuo* and finely powd.: N 32, T 16.1-285.9°, C_p 0.680-6.390; *grape sugar*, pure, coarse powder: N 30, T 19.9-287.2°, C_p 0.0848-2.157; *ketone resin* $(\text{C}_{11}\text{H}_{10}\text{O})$, amorphous, celluloid-like, in 3 mm. cubes: N 16, T 72.6-298.4°, C_p 0.651-2.319; 2nd sample: N 5, T 17.5-78.3°, C_p 0.107-0.685; *glycerol*, amorphous, 1.3% water: N 36, T 18.8-294.4°, c 0.0180-0.5817 (where c is the sp. heat of the moist glycerol). In all cases except that of NH_4Cl , C_p increases continuously with increasing temp. In the case of NH_4Cl , the mol. heat is very nearly the same as that for NaCl until $T = 80^\circ$. Hence NH_4 seems to vibrate like 1 atom. From $T = 140^\circ$ up to $T = 243^\circ$, the mol. heat of NH_4Cl increases more rapidly than for the alkali chlorides. When $T = 242.6^\circ$, $C_p = 2.109$. When $T = 260.4^\circ$, $C_p = 3.123$ and rises normally from that temp. The abnormality when $T = 243^\circ$ is ascribed to the change of vibration of NH_4 from that similar to 1 atom to the vibration as 5 atoms. The at. heat of glycerol near 180° abs. shows a very sharp increase. This is associated with its softening.

F. E. BROWN

The establishing of the absolute temperature scale below the melting point of ice. F. G. KEYES, B. TOWNSEND AND L. H. YOUNG. *J. Math. Phys. Mass. Inst. Tech.* **1**, 243-312(1922).—A discussion of the const. vol. gas thermometer and its error is given. The exptl. results in the study of the equation of state of Keyes indicates that the pressure is a

linear function of the temp. at const. vol., provided there is no association or dissociation. Direct exptl. verification of the fact that the const. vol. gas thermometer *needs no thermodynamic correction* has been obtained by establishing the measured temp. with a N_2 const. pressure thermometer as independent of the initial ice point pressure over a considerable range and for which corrections may be accurately calcd. by the Keyes equation of state. The value of the b. p. of S , 444.55° from the const. pressure N_2 thermometer (corrected), is accurately checked by He , H_2 and N_2 const. vol. thermometers *without thermodynamic corrections*. The const. vol. H_2 and N_2 thermometric scales are exptly. compared. The deviations become measurable at -70° and increase to 0.6° at the b. p. of O_2 . This divergence can be readily explained by the combined effects of association of the N_2 and its adsorption upon the walls of the quartz container. He is found to diffuse too readily through quartz at room temp. to permit of its convenient use in a thermometer bulb of this material. H_2 , likewise, diffuses at ordinary temps., but so slowly as not to interfere with its use in quartz for low temp. thermometry. A *Cu-constantan thermocouple* is found satisfactory in the permanence of its indications over the range 0° to -183° and by direct comparison with the H_2 thermometer is found to have an e. m. f.-temp. relation of the form $e = at - bt^n$, (a , b , n , const.). The *Pt resistance thermometer* used in conjunction with the Callendar formula gives values increasingly too low as the temp. is reduced, the deviation amounting to about 1.6° at the b. p. of O_2 —its exact value depending, however, upon the particular instrument employed (being due, possibly, in part, to strains set up in the wire which contracts on its supporting frame). By means of a calibrated multiple Cu-constantan thermocouple and a Pt resistance thermometer the following f. ps. are established to serve as *fixed points for secondary thermometer calibration*: CCl_4 , -22.87° ; Hg , -38.90° ; C_6H_5Cl , -45.58° ; $CHCl_3$, -64.19° ; NH_3 , -77.80° ; $C_2H_5CH_3$, -95.70° ; CH_2Cl_2 , -98.39° ; CH_3OH , -98.54° ; CS_2 , -112.97° ; $(C_2H_5)_2O$ mod. I, -123.40° ; $(C_2H_5)_2O$ mod. II, -115.9° . By means of the vapor pressure method the b. p. of CO_2 is found to be -78.53° and that of O_2 $-182.94^\circ C$.

G. I. CLARK

The equation of state for methane gas phase. F. G. KEYES, L. B. SMITH AND D. B. JOUBERT. *J. Math. Phys., Mass. Inst. Tech.* 1, 191-210(1922).—A new app. is described for *measuring by the isometric method, the pressure-vol.-temp. properties of a gas* whose crit. temp. is below 0° . The isometrics of CH_4 are linear within the limits of exptl. error between 0° and 200° up to 300 atms. The *Keyes' equation* represents the pressure-vol.-temp. relations accurately. The equation is, for units atm., cc./g., degrees abs.: $p = [4.1175/(v - b)]T - [9802/(v + 0.565)^2]$, where $\log_{10} b = 0.56195 - (1.05/v)$. The wt. of a l. of CH_4 calcd. by the equation of state is 0.7718 at 0° and 760 mm. The coeffs. of temp. expansion at 1 atm. obtained from the equation of state are 0.0036796 at const. vol. and 0.0036834 at const. pressure.

R. S. TAYLOR

The thermodynamic properties of methane. F. G. KEYES, R. S. TAYLOR AND L. B. SMITH. *J. Math. Phys., Mass. Inst. Tech.* 1, 211-42(1922); cf. preceding abstract.—From the exptl. values of the v. ps. and densities of liquid CH_4 detd. over the entire liquid phase region by precision methods described in detail, a no. of equations and thermodynamic consts. are derived: (1) an equation for v. p. as a function of abs. temp., $\log_{10} p(\text{atm.}) = -(595.546/T) + 8.09938 - (4.04175 \times 10^{-2}T) + (1.68655 \times 10^{-4}T^2) - (2.51715 \times 10^{-7}T^3)$; (2) a mean density equation for calcg. vapor densities near the crit. point, $D_m = 0.16134 + 0.00065723(T_c - T)$; (3) crit. temp. 191.03° abs., crit. pressure 45.8 atm., crit. vol. 6.2 cc./g.; (4) an equation for the heat of evapn. λ , from 100° to 150° abs., $\log_{10} \lambda = 1.65214 + 2.0076 \times 10^{-4}(T_c - T) + 0.22225 \log_{10}(T_c - T)$; (5) a linear relationship involving the internal energy change and the sp. vol. of liquid CH_4 ; (6) an equation for the sp. heat of the vapor as a function of temp. and low pressure, $C_{p1} = 0.4288 + 1.12 \times 10^{-3}T - 6.45 \times 10^{-7}T^2 + 13.04 \times 10^{-10}T^3 +$

$(93/T^2)p$; (7) the calcn. from (6) and the usual thermodynamic equations of the sp. heat of the liquid near the b. p. as 0.82 cal./g. G. L. CLARK

The third law of thermodynamics. Evidence from the specific heats of glycerol that the entropy of a glass exceeds that of a crystal at the absolute zero. G. F. GIBSON AND W. F. GILVUŠ. *J. Am. Chem. Soc.* **45**, 93-104 (1923); cf. *C. A.* **14**, 2880, 2881.—An extremely effective and accurate *vacuum-inclosed aneroid calorimeter* is described; the heating- and temp. measuring-coil, wound on the calorimeter, is of Cu to avoid differential expansion. Gold leaf gives a very closely adherent surface of low radiating power. The greatest improvement is an elec. heated heavy copper inclosing cylinder, which, being in the vacuum, gives an easily controlled and very uniform and constant environmental temp. The max. discrepancy of any result from a smooth curve was 0.5%. The results leave hardly a chance for doubt that glycerol glass has an entropy of more than 0 at 0° K. 5.6 ± 0.1 cal./deg. per mol. is the value indicated. A rather sudden increase of nearly 100% occurs in the true specific heat of amorphous glycerol just below 190° K., probably associated with a liquefaction, or softening of the glass. Glycerol can be crystd. by very slow heating from liquid air temps. The latent heat of fusion is 4370 cal./mol., at 291.00° K. W. P. WHITE

The chemical constant of some diatomic gases. J. R. PARTINGTON. *Phil. Mag.* **44**, 983-93 (1922).—By a method of calcn. based on generalized statistical mechanics and the quantum relation, P. deduces a formula for the chem. const. (C) of diatomic gases $C = 2.5 \log M + 2 \log K + 12.730$, in which M is the mol. wt., and where for the case considered $K^2 = r^2$, where r is the radius of the mol. The value of C calcd. for O_2 is 1.001, for N_2 0.904, for H_2 -2.255, for CO 1.205, for NO 1.263. Comparison is made with the corresponding values of Nernst and of Langen. S. C. L.

Application of the Nernst heat theorem to dilute solutions. K. F. HERRZFELD. *Z. Elektrochem.* **28**, 460-3 (1922).—A mathematical paper. The differences between the "bound-energies" of gram-ion solns. of 19 different ions and that of a gram-ion soln. of Ag^+ (i. e., $(1/v)(G_x - G_{Ag})$, where v is the valence of the ion x , and $G = U - U_0 + A - A_0$, where U and A refer as usual to total and free energies, resp.) have been calcd. either from normal potentials or the solubilities of slightly sol. salts of the ions. With the aid of Nernst's heat theorem, the potentials have been calcd. of those metals whose G values were detd. from solubilities, e. g., $Ca = -2.89$. From the G values for a no. of difficultly sol. metal halides, values have been calcd. for $2RT \ln C$ (where C is the chem. const.) for each of the halides. The values so obtained agree, on the whole, fairly closely with those detd. by expt. The results of the investigation show that the *solv. of salts* can be calcd. from normal potentials by means of Nernst's heat theorem. H. JERMAIN CREIGHTON

Activities of the ions of potassium hydroxide in aqueous solutions. MAX KNOBL. *J. Am. Chem. Soc.* **45**, 70-7 (1923); cf. *C. A.* **14**, 1072.—A revision of the work of Chow. The e. m. fs. of cells of the type $H_2 | KOH(c_1) | KHg_x | KHg_x | KOH(c_2) | H_2$ have been measured at 25° for concns. of KOH between 3 N and 0.001 N . The activity coeffs. of the soln. and the free energies of diln. between various concns. have been calcd. C. R. PARK

Transference numbers of potassium hydroxide in aqueous solutions. M. KNOBL. D. K. WORCESTER AND F. B. BRIGGS. *J. Am. Chem. Soc.* **45**, 77-9 (1923).—The e. m. fs. of concn. cells of the type $H_2 | KOH(c_1) | KOH(c_2) | H_2$ have been measured at 25° for concns. between 3.0 N and 0.01 N . These values together with the values given in the paper abstracted above have been used to calc. the transference no. of the K ion in KOH solns. at various concns. The transference no. of the K ion is const. and equal to 0.2633. C. R. PARK

Potential difference between glass and electrolytes in contact with the glass. W. S. HUGHES. *J. Am. Chem. Soc.* **44**, 2860-7 (1922).—A p. d. exists between glass surfaces

and solns. in contact with them. The variation in this potential is approx. the same as the variation in the H electrode potential, but is only approx. a linear function of the latter. This variation may be made the basis for a method of *electrometric titration* for solns. contg. oxidizing agents which would render a H electrode useless. C. R. P.

Thermo-electromotive force of copper-manganese alloys. SKEZUG KIMURA AND ZUNEHACHI ISAWA. *Phys. Rev.* 20, 441-51(1922).—The thermo-elec. behavior of a series of Cu-Mn alloys against pure Cu has been investigated for the range 0° to 100°. The Mn used to make the alloys contained about 2% Fe. The curves conform to the general equation $E = \alpha t + \beta t^2$, when α and β are consts. Some of these alloys are positive and others negative to the pure metal. Some revision should be made in the electronic theory of conduction to account for this phenomenon. C. R. P.

Conduction process in ordinary soda-lime glass. C. A. KRAUS AND E. H. DARBY. *J. Am. Chem. Soc.* 44, 2783-97(1922).—The replacement of Na in glass by other metallic elements has been accomplished by electrolysis. The anode from which the metallic element enters the glass may be either an amalgam or a fused salt. Usually the glass so formed by substitution of the second metal is unstable. Na has been replaced by Ag to a depth of about 0.1 mm. The speed of the ions increases greatly with the temp. The cond. of glass is due entirely to the movement of the metallic Na ions. About 75% of the ions are in a condition to conduct. The rest apparently are held rigid.

C. R. PARK

A special class of cells. VASILESCO KARPEN. *Compt. rend.* 175, 96-8(1922).—A Cu block, with a cavity 32 mm. in diam. and 35 mm. in height, was carefully fitted with a Cu piston which was sepd. from the walls of the cavity by mica. Ten cc. of CuSO_4 soln. was placed in the cell and subjected to temp. changes. Between 250° and 350°, 2 phases were noted and the c. m. f. showed a max. of 0.250 v. The internal resistance ranged from 1000 to 20000 ohms. A cell with Zn electrodes and a mixt. of H_2O , amyl alc. and ZnSO_4 showed an c. m. f. as high as 0.7 v. Smaller amts. of ZnSO_4 gave lower values of c. m. f. Cells contg. H_2O and amyl alc. with Fe peptonate gave an c. m. f. which ranged from 0.4 to 0.6 v. The results of these observations seemed to show that these cells do not act in accord with *Nernst's theory of osmotic phenomena*.

DWIGHT T. EWING

Salt nature of sodium ethyl; indirect electrolysis of zinc ethyl. F. HEIN. *Z. Elektrochem.* 28, 469-71(1922).— $\text{Zn}(\text{C}_2\text{H}_5)_2$ is a very poor elec. conductor; but a soln. of NaC_2H_5 dissolved in $\text{Zn}(\text{C}_2\text{H}_5)_2$ behaves like a soln. of a typical electrolyte, and conducts the elec. current as well as 0.1 N KCl. Electrolysis takes place at a relatively low voltage. The end-effect of the electrolytic process is an indirect electrolysis of $\text{Zn}(\text{C}_2\text{H}_5)_2$. On covering the top of the soln. of NaC_2H_5 in $\text{Zn}(\text{C}_2\text{H}_5)_2$ (in which the electrodes are) with a layer of pure $\text{Zn}(\text{C}_2\text{H}_5)_2$, it is found that this upper layer decreases after electrolysis has continued for a long period. The quantity of $\text{Zn}(\text{C}_2\text{H}_5)_2$ in the lower layer remains unchanged. These results indicate the probable salt-nature of NaC_2H_5 and that only Na^+ and C_2H_5^- exist in the soln.

H. JERMAIN CREIGHTON

Determination of absolute electrode potentials. ALLEN GARRISON. *J. Am. Chem. Soc.* 45, 37-44(1923).—A Ag needle at its iso-elec. point is used as a zero electrode in the detn. of the abs. potential of the calomel electrode. The value found at 25° for the 0.1 N calomel electrode is between -0.20 and -0.10 v. C. R. PARK

Measurements of electrode potential drop with direct current and alternating current electrolysis. S. MARSH AND A. F. EVANS. *Proc. Roy. Soc. (London)* 102A, 328-40(1922).—The variation with time of the electrode potential drop has been examd. for both d. c. and a. c. Electrodes of bright Pt, platinized Pt, Au, and Ni were used. The variations in potential drop are found to be in accordance with those which might be predicted from the deposition of gases or the formation of an oxide coat upon the

surface of the metal. In the case of the d. c. measurements, for example, the type of potential-time curve is the same for all the metal cathodes, being a gradual increase with time up to a definite satn. potential. The explanation of this phenomenon is that the gas entering the electrode surface sets up a back e. m. f. which increases with increasing quantity of gas until the metal surface becomes satd. Since Au occludes the gas in smaller quantity than Pt the total potential drop increase is less for Au than for Pt. Because of the larger surface of the platinized Pt the satn. point is reached less quickly than with bright Pt.

C. R. PARK

Chemical reactions provoked by the corona effect in circuits through which continuous currents are passed. (Preliminary note.) C. MONTEMARTINI. *Gazz. chim. ital.* 52, II, 96-7(1922).—This paper enumerates some reactions obtained by means of the corona effect. The app. consisted of a transformer (240,000 v.) connected to a synchronous commutator C and this to S a "spinterometer" (plate and point) by means of a 30 mm. Cu tube. A fine metallic thread 1 m. long and contained in a glass tube joins S and the other end of the secondary of the transformer. In this the corona effect is produced by regulating the current flowing through S and the resistance on the primary of the transformer. Currents of 5-6 milliamps. and 185,000 v. were used. After 2 hrs. use the temp. in the glass tube was raised $\pm 1^\circ$. The following reactions were found to occur: O_3 formation in air; $2CO_2 \longrightarrow 2CO + O_2$; $N_2 + 3H_2 \longrightarrow 2NH_3$; $CO + H_2O \longrightarrow CO_2 + H_2$; $C_2H_2 + N_2 \longrightarrow 2HCN$; $CO_2 + 2H_2 \longrightarrow HCHO + H_2O$; $C_2H_6 + CO_2 \longrightarrow PhCO_2H$; $H_2S \rightleftharpoons S + H_2$; $2SbH_3 \rightleftharpoons 2Sb + 3H_2$. Quant. details will be published later.

E. J. WITZEMANN

The minimum discharge potential in gases at low pressures. E. DUBOIS. *Compt. rend.* 175, 947-9(1922); cf. *C. A.* 15, 3932.—The min. voltage required for discharge in H between W, Mo, and Pt electrodes is much greater when the cathodes have first been heated to a white heat. This difference D. attributes to compds. present on unheated surfaces. By vaporizing small quantities of alkali chloride (10^{-6} g. per sq. cm.) on a heated electrode, voltage likewise drops. For heated electrodes potential is apparently independent of metal.

BENJAMIN S. NEUHAUSEN

The dielectric strength of lipoids and solids. A. GÜNTHER-SCHULZE. *Jahrb. Radioakt. Elektronik* 19, 92-112(1922).—The dielec. strength is defined as the minimum potential drop which causes a spark to pass through the dielectric. In explaining the mechanism by which the discharge occurs, G.-S. assumes the presence of ions in every liquid. These are accelerated by the applied field and in moving through the liquid generate sufficient heat to leave paths of vapor behind. Other moving ions strike these mols. in the vapor state, causing ionization by which the spark is propagated. The dielec. strength will depend on (1) size of the ions, (2) viscosity of the liquid, (3) heat of vaporization of the liquid, (4) d. of the vapor and (5) ionization potential of the vapor. By this theory G.-S. accounts for the following exptl. facts for liquids: (1) increase of dielec. strength with pressure; (2) that dielec. strength is greater for a. c. than for d. c.; (3) that dielec. strength does not change with the cond.; (4) that in some cases there is a temp. where the dielec. strength is a max.; (5) that the dielec. strength is greatly changed by the presence of solid suspensions. In the case of solids the lack of homogeneity renders the interpretation of the mechanism from meager exptl. data very difficult. A bibliography is given.

J. A. ALMQUIST

Second undamped wave method of determining dielectric constants. A. P. CARMAN AND G. T. LORANCE. *Phys. Rev.* 20, 715-7(1922); cf. *Hyslop and C. (C. A.* 16, 4124).—A revision of former method. Values for air, CO, and illuminating gas at 760 mm. are 1.00060, 1.00099, and 1.00077, resp.

C. R. PARK

A quantum theory of the thermal conductivity in non-metallic crystals. YOSIYOSI ENDO. *Sci. Repts. Tohoku Imp. Univ.* 11, 183-93(1922).—Other theories are unsatis-

factory. The present one in the form it now has also gives very poor agreement with expt. W. P. WHITE

A spectroscopic method of studying the formation of complex salts in dilute solutions. YUJI SHIBATA, TOSHI INOUE AND YUICHI NAKATSUKA. *Japan J. Chem.* 1, 1-18(1922).—An English translation (cf. *C. A.* 16, 2075). K. K.

The magnetic susceptibility of six nitrogen oxides. TAKÉ SONÉ. *Sci. Repts. Tohoku Imp. Univ.* 11, 139-57(1922).—Three of these were obtained for the first time in a trustworthy way. The results were, for sp. susceptibility $\times 10^6$: (paramagnetic) O_2 , 104.1; NO 48.8; NO_2 4.5; (diamagnetic) N_2 , -0.27; N_2O , -0.43; N_2O_4 , liquid, -0.21; N_2O_4 , liquid, -0.28; N_2O_5 , solid, -0.03. N_2O gave practically the same value, whether liquid or gaseous. W. P. WHITE

Magnetic analysis of the stannic acids. PAUL PASCAL. *Compt. rend.* 175, 1063-5 (1922).—Magnetic analysis shows that the stannic acids are simply *hydrogels* of the anhydrous stannic oxide. J. A. ALMQUIST

The properties and uses of carbon tetrachloride. G. GORI. *Boll. chim. farm.* 61, 641-8(1922).—Mainly a review of the applications of CCl_4 in the industries and in medicine. In the chem. lab. its use is suggested in place of the customary solvents employed in the color tests for I and Br, indican and urinary pigments, extn. of alkaloids in toxicological work, and extn. of caffeine, theobromine, cholesterol, etc. Expts. with guinea pigs show that CCl_4 is far less active as an anesthetic than $CHCl_3$.

A. W. DOX

The importance of "impurities." JEROME ALEXANDER. *Ind. Eng. Chem.* 15, 190-1(1923).—A. cites many instances taken from the fields of disease-prevention, zymology, catalysis, metallurgy, etc., to illustrate the profound influence exerted by minute traces of impurities. E. G. R. ARDAGH

An analysis and comparison of systems of color measurement; a proposed arrangement for measured colors; and some notes on interchangeability in color measurement. H. S. BUSBY. *Proc. Am. Soc. Testing Materials* 22, II, 504-14(1922). E. J. C.

Artificial daylight [for color matching]. F. E. LAMPLOUGH. *J. Soc. Dyers Colourists* 38, 265-9(1922).—The various sources of artificial daylight are discussed in relation to their value for color matching with particular reference to Chance's daylight glass. Curves showing the comparative intensity of the various lights at different parts of the spectrum are given. CHAS. E. MULLIN

Heat of dissolution of thallosulfate. FUSAO ISHIKAWA. *J. Chem. Soc. Japan* 43, 560-76(1922).—Heat of dissoln. (F) of Tl_2SO_4 at 30° was detd. by 2 different methods. (1) By detg. e. m. f. of two cells: (A) $Tl-Hg$ |satd. soln. of Tl_2SO_4 with solid $[Hg_2SO_4|Hg]$; (B) $Tl-Hg$ |satd. soln. of Tl_2SO_4 | $Hg_2SO_4|Hg$. Then $(F)_{T^\circ} = T_0 [(dE/dT)_{T_0} - (dE/dT)_{T^\circ}]_{T^\circ} \times 2 \times 9649 \times 0.2389$. The measured e. m. f. were: $(dE/dT)_{30.4} = +0.00032$ v per degree C. and $(dE/dT)_{30.9} = +0.00852$ v per degree C. and from these $(F)_{30}$ was calcd. to be -14.75 gram cal. per g. (2) By detg. e. m. f. of concn. cells, and soly. of Tl_2SO_4 ($F)_{30}$ was calcd. according to $(F)_{T^\circ} = T_0 (dE/dC)_{T^\circ} (dC/dT)$ ($2 \times 96494 \times 0.2389$) where $dE/dC =$ change in e. m. f. according to concn., and dC/dT is soly. change with temp. thus $(F)_{T^\circ} dC/dT$ was calcd. from Berkeley's data (*Phil. Trans.* 211), and found to be $(dC/dT)_{30} = +0.009964$ mol. per degree C. or $+0.1387$ g. per degree C. dE/dC was measured for concns. of 2.283 g. per 100, 3.059 g., 4.104, 5.110 and 5.826 (satd.). $(dE/dC)_{5-30}$ was found to be -0.003791 v. per 1% change in concn. From these data, $(F)_{30}$ became = -14.58 g. cal. per g. S. T.

Standard Weston cells (ISHIBASHI) 4. Perkin Medal award, 13. Flocculation of soils (COMBER) 15. Activation of contact Pt by Röntgen rays (SCHWARZ, KLINGENFUSS) 3.

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SMALLWOOD, JULIAN: **Mechanical Laboratory Methods.** Revised Ed. New York: Van Nostrand Co. 423 pp. \$3.50. Reviewed in *J. Western Soc. Eng.* **27**, 223(1922).

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Doctor Aston's experiments on the mass spectra of the chemical elements. C. G. ABBOT. Smithsonian Inst., *Ann. Rept.* 1920, 223-40(1922).—Extracts from Aston's papers (*C. A.* **14**, 688 and 3578) with an introduction by Abbot. W. F. MEGGERS

Spectra of sparks in water. LEON BLOCH AND EUGENE BLOCH. *J. phys. radium* **3**, 309-25(1922).—A more detailed account of work reported in *C. A.* **16**, 3037.

K. B.

The atoms of matter; their size, number, and construction. F. W. ASTON. *Nature* **110**, 702-5(1922).—An address. NORRIS F. HALL

Atomic weight of boron. F. H. LORING. *Chem. News* **125**, 239(1922).—Using his method of calcg. at. wts. (*C. A.* **14**, 2580), L. finds that of B to be 10.77. The proportions of the isotopes of wt. 10 and 11 are supposed to be 2¹:3¹. This value is in approx. agreement with the latest exptl. value, 10.82. JAMES M. BELL

Bohr model of the hydrogen molecules and their magnetic susceptibility. KÔTARÔ HONDA. *Nature* **110**, 664(1922).—Contrary to the general impression, Bohr's model of H₂ does not show paramagnetism when investigated by Langevin's theory, but diamagnetism in harmony with expt. On the 2 simplest assumptions (that the azimuthal and radial quantum nos. are = 1, 0 and 1, 1, corresponding, resp., to circular and elliptic orbits) H. calcs. the magnetic susceptibility (χ) = -0.712×10^{-6} and -5.70×10^{-4} . If H₂ consists of 35 and 65%, resp., of mols. of the 2 kinds, the calcd. χ coincides with Sone's (obs.) value 3.96×10^{-4} . NORRIS F. HALL

Positive-ray analysis of potassium, calcium and zinc. A. J. DEMPSTER. *Phys. Rev.* **20**, 631-8(1922).—The app. and methods previously described (*C. A.* **12**, 1724) for detg. the isotopes of elements by positive-ray analysis were used to det. the isotopes of K, Ca and Zn. For K, isotopes with at. wts. 39 and 41 were found, verifying Aston's results. The ratio of the intensities of the two is 18:1, yielding for the av. at. wt. a value of 39.10, in agreement with that found by chem. methods. For Ca, two isotopes of wts. 40 and 44 in the intensity ratio 70:1 were found. The at. wt. derived for Ca is 40.055 compared with the chem. value of 40.07. When the detn. of the relative proportions of all the isotopes of an element is made sufficiently accurate and reliable, comparison between calcd. and observed av. at. wts. should give a measure of the packing effect or divergence of the wts. of the isotopes from integral values. Four isotopes of Zn of wts. 64, 66, 68 and 70 were observed, with faint indications of another at 67. No intensity ratios or detns. of the av. at. wts. are given. Improved resolving power of the app. should make it possible to analyze the isotopes of elements up to at. wt. 100. C. C. KRASS

Formation of helium and neon in Geissler tubes containing hydrogen. A. PIUTTI. *Z. Elektrochem.* **28**, 452-3(1922).—In 70 expts. carried out under different conditions, no spectral lines have been obtained corresponding to the D_1 line of He or the D_1 line of Ne.

H. JERMAIN CREIGHTON

Isotopes of iron. F. H. LORING. *Chem. News* **125**, 239(1922).—In an earlier paper (*C. A.* **14**, 3356) the isotopes of Fe are supposed to have weights 54 and 56, values which agree with Aston's recent results (*C. A.* **16**, 4136).

JAMES M. BELL

Isotopes of antimony. F. W. ASTON. *Nature* **110**, 732(1922).—The mass spectrum using $SbMe_3$ shows 2 lines of nearly equal strength at 121 and 123. These results show that 120.2 is certainly too low for the at. wt. of Sb, but are in excellent agreement with the value 121.77 recently obtained by Willard and M'Alpine.

A. B. STEARN

Separation of the isotopes of zinc. A. C. EGERTON. *Nature* **110**, 773(1922).—By distn. in high vacuum with liquid-air condensation and careful regulation of the temp. and quantity distd. some sepn. was effected. With the density of the original Zn as unity, that of the distillate was 0.99971 and of the residue 1.00026 as an av. of 7 detns. The max. variation was 0.00015. This indicates 3.5 units in second place of at. wt. which is less than if the metal were composed of equal parts of an isotope of wt. 64 and a mixt. of wts. 66, 68 and 70.

A. E. STEARN

Isotopes of selenium and some other elements. F. W. ASTON. *Nature* **110**, 664(1922).—The element itself when vaporized in the discharge tube gave a clear mass-spectrum. There are six isotopes, of masses 74(f), 76(c), 77(e), 78(b), 80(a), 82(d). The intensities are in the order of the letters and agree with the accepted at. wt. 79.2. No deviation from the whole no. rule is detectable. Cd and Te gave no results, but incidentally it was settled that Cl has no isotope 39, and Al is a simple element 27. Two new Xe lines were found at 124 and 126, making nine in all for this element. Xe 124 is isobaric with Sn, and Se 78, 80, 82 are isobares of Kr. All known isobares have even at. wt.

NORRIS F. HALL

Mesothorium. HERMAN SCHLUNDT. *Bur. of Mines, Tech. Paper* **265**, 55 pp. (1922).—A paper on the properties and production of Meso-Th. The history and disintegration of the Th series are given. Meso-Th is compared with Ra for use in luminous paints and therapeutics. The extn. of Th and Meso-Th from monazite sand is given. S. gives a good description of the treatment of the concentrates and the crystn. of Meso-Th. A comparison of the α - and γ -ray activity of Meso-Th and Ra is made.

L. D. R.

Recent experiences in testing radioactive preparations. W. BOTHE. *Z. Elektrochem.* **28**, 459-60(1922).—A brief account of the recovery of 2 radioactive preps.: one of 11 mg. which was lost in the sewer of a clinic; the other of 110 mg. Ra, the container of which exploded scattering the contents.

H. JERMAIN CREIGHTON

The action of radium rays on cyclohexene. N. ZÉLINSKY. *Rec. trav. chim.* **41**, 613(1922).— $RaBr_2$ contg. 0.0005-0.0006 g. Ra was placed in a sealed tube with 1.5 cc. C_6H_{10} . A year later a black deposit of C was noticed on the grains of the Ra salt which increased with time. The hydrocarbon became dark yellow in color and contained simpler hydrocarbons as well as dehydrogenated hydrocarbons. C. thinks it possible that an analogous process takes place during the formation of petroleum in nature.

E. J. WITZEMANN

Theory of scattering of corpuscular rays. GREGOR WENTZEL. *Physik. Z.* **23**, 435-6(1922).—The probabilities of all possible tracks of scattered particles are calcd. on W.'s (unpublished) theory of multiple scattering, and integrated graphically over all forms of paths. The calcns. are compared with the measurements of Crowther and Schönland (*C. A.* **16**, 1535) on β -ray scattering in gold foils, and satisfactory agreement is obtained.

NORRIS F. HALL

Analysis of α -ray photographs. P. M. S. BLACKET. *Proc. Roy. Soc. (London)* **102A**, 294-317 (1922).—The method of C. T. R. Wilson for making visible the tracks of ionizing particles was used to study the passage of α -particles through air and A. Especial attention was directed to the collision of the particles with the nuclei of the atoms. The theory of the occurrence of such collisions assumes a law of force varying inversely as the square of the distance. Other investigations have indicated a departure from this law when the nucleus and the α -particle are close together. At sufficiently great distances there is also a departure because of the screening of the nucleus by the electrons. The method of procedure is the same as that outlined by Shimizu. A statistical study of the frequency of the sudden bends in the tracks in both air and A showed that the velocity of the particles very close to the end of the track is as low as one twentieth of the original velocity. These are very slow α -particles compared to those previously observed. This min. velocity is about the velocity at which the α -particle loses its ionizing power in air. The observed distribution of the bends is consistent with the hypothesis that the inverse square law of force holds between the nucleus and the α -particles when their distance apart lies between 7×10^{-12} and 10^{-9} cm. in the case of A and 5×10^{-12} and 5×10^{-16} in the case of air. It appears possible that there is, especially in the case of A, a departure from the inverse square law at distances greater than those given. A study of the rare collisions in which an α -particle sets an at. nucleus in motion, thus giving a branched track, shows that collisions between α -particles and nuclei appear to be perfectly elastic. A. W. SMITH

The collisions between α -particles and atomic nuclei. PIERRE AUGER and FRANCIS PERRIN. *Compt. rend.* **175**, 340-3 (1922).—The tracks of α -particles in different gases were studied by the condensation method of C. T. R. Wilson, using 2 cameras placed at right angles. Measurements of 52 tracks in argon permitted a calcn. of its at. no. The result was 19 instead of 18. Measurements were made also in H and in H mixed with air. FARRINGTON DANIELS

A study of the fall of potential in a plate condenser during ionization by alpha particles. M. ARTNER. *Sitzb. Akad. Wiss. Wien.* **130**, IIa, 253-64 (1921).—See C. A. **16**, 1703. D. C. B.

Branchings and sharp bends in the tracks of beta particles. W. BOTHE. *Physik. Z.* **23**, 416 (1922).—A large no. of stereoscopic photographs of β -ray tracks were taken by the Wilson cloud method. Eight of the pictures clearly showed branching. The branches were coplanar with the main tracks and made an angle of about 90° with them. The more deflected branch was always shorter and thicker. The branching is thought due to displacement, through collision, of a slowly moving, weakly bound electron. Sharp bends in the tracks (due to close approach to nuclei) were also observed, but the β -particles lose relatively little energy when they are deflected. The small spurs seen on α -particle tracks are lacking. B. thinks the β -particle tracks are not smooth curves, but broken lines, due to successive small deflections. NORRIS F. HALL

The emission of light in the glow discharge. R. SERLIGER. *Ann. Physik* **67**, 352-8 (1922).—The light emitted in various parts of the glow discharge was measured with a spectrograph and a microphotometer. Electrodes of Fe, Al and Hg were used. H₂, N₂, O₂ and A were studied. FARRINGTON DANIELS

Relation between photoelectric current and illumination, on very thin layers of potassium. H. GERTL. *Ann. Physik* **67**, 420-7 (1922).—If the P wire of a K photoelec. cell is made the cathode, a slight current is generated when it is illuminated. It is due to the presence of a very thin film of K, condensed on the wire, even though the vapor pressure of K is very low. This is proved by the loss of sensitivity and its slow return after heating the wire. In general, the photoelec. current is proportional to the intensity of light, but with very thin layers, it was thought that this proportionality would

fail after reaching a sufficiently great illumination. Careful expts. showed, however, that the two were strictly proportional throughout the whole range studied. The work is being continued with improved app.

FARRINGTON DANIELS

Concerning the relation between mass and the absorption of cathode rays of medium velocity. A. BECKER. *Ann. Physik* **67**, 428-61 (1922).—B. has detd. carefully the absorption of cathode rays by various gases. All the elements investigated (H, C, Cl and Br) show a sp. action. The absorption does not depend on the mass alone. The deviation from the mass relation is greatest for H and least for C. These deviations of the elements occur in all their compds. Several hydrocarbons, including some isomers, were studied. The influence of mol. structure on the absorption of cathode rays is barely detectable.

FARRINGTON DANIELS

The arc light as a rectifier. STANISLAW BOROWICK. *Z. Physik* **23**, 362 (1922).—With a. c. an arc between an electrode of iron oxide and one of C is formed only when the iron oxide is positive. The arc will not strike between 2 electrodes of iron oxide. Positive ions are emitted by heating the oxide to a high temp. At 100° and 110 v., the positive current amounts to several milliamps.

FARRINGTON DANIELS

The existence of high-mobility ions. OSWALD BLACKWOOD. *Phys. Rev.* **20**, 499-504 (1922).—Nolan (*C. A.* **16**, 198) using a modified air-blast method found ions in air having mobilities 7 times that ordinarily observed, and also found 8 widely sep. sizes of ions. B. with Nolan's app. found irregular ion mobility curves like Nolan's but failed to get the series of repeatable breaks indicating the 8 sep. classes of ions. By substituting the uneven gas flow produced by gasometers by a uniform air blast from a rotary blower, all the irregular breaks disappeared. The curves then indicated a single class of ions of high mobility. Low voltage intercept of the ion mobility curves giving the high mobilities was due to the presence of a vol. ionization throughout the chamber caused by secondary X-rays from the radioactive sources. With Po instead of emanation tubes as a source of ionization the curves gave intercepts with the voltage axis yielding mobilities close to the values which have been observed by all previous workers except Nolan.

L. B. LOEB

Mobilities of electrons in hydrogen. L. B. LOEB. *Phys. Rev.* **20**, 397-404 (1922).—Using the Rutherford a. c. method as described in a previous paper (*C. A.* **16**, 1360) with the high-frequency oscillations from an audion oscillator, L. detd. the mobilities of electrons in H₂. The technic of the first paper giving the results of measurements in N₂ was improved. The results of the mobility measurements in H₂ may be closely summed up in the form of the general equation $K = (6.67 \times 10^3) / [97.2 + (V_0/d)(760/p)^{1/4}]$. Here K is the mobility const. of the electrons computed from the voltage intercept V_0 of the mobility curve by the equation, $K = (\pi/\sqrt{2})(nd^2/V_0)(p/760)$, n is the frequency of the alternating potential, d is the plate distances used, (2.025 cm.), and p the pressure in mm. This equation differs from the one found for N₂ in form, only in that the quantity $760/p$ is here raised to the $3/4$ power instead of to the first power as in the case of N₂. This difference is ascribed to the crudities of the technic in the earlier measurements. The equation above differs from the theoretical form predicted by Townsend for electron mobilities, owing to a change in either the mean free path of the electron or its elasticity of impact with velocity in accordance with expts. by Townsend. Comparison of the mobility of electrons as detd. from the above equation for very small values of the field, with the mobility computed for the electrons assuming a mean free path as given by the kinetic theory, give the observed mean free path as 0.53 of the assumed one. In N₂ the observed free path was found to be 3.9 times the assumed one. [The equation given in the abstract is not the equation given in the original paper, since the latter contains a serious numerical blunder which is being rectified, ABSTRACTOR.]

L. B. LOEB

The thermal ionization of gaseous elements at high temperatures. A. A. NOYES and H. A. WILSON. *J. Am. Chem. Soc.* **44**, 2806-15(1922); cf. *C. A.* **17**, 22.

W. ALBERT NOYES, JR.

A spectroscopic investigation of the ionization of argon by electron collisions. FRANK HORTON and ANN C. DAVIES. *Proc. Roy. Soc. (London)* **102A**, 131-50(1922); cf. *C. A.* **14**, 3361; **16**, 2262.—The min. radiation voltage for A is found to be 11.5 and that for simple ionization is 15.1. Double ionization occurs by single collision at 34 v., while a simply ionized atom may be ionized at $34 - 15 = 19$ v. The "blue" spectrum appears at 19 v., increases in intensity to 24 v., does not change further till 34 v., when it increases suddenly in intensity. The ionization potential at 15.1 v. is probably related to the M X-ray absorption limits of the elements in the same way as that of He is related to the K series and that of Ne (16.7 v.) to the L series.

W. ALBERT NOYES, JR.

The molecular scattering of light in vapors and in liquids and its relation to the opalescence observed in the critical state. K. R. RAMANATHAN. *Proc. Roy. Soc. (London)* **102A**, 151-61(1922).—The Einstein-Smoluchowski formula for light scattering is found to hold good in the case of ether in the liquid form from 30° to the crit. temp. (193.6°) and in the gaseous phase to 217° , except in the immediate neighborhood of the crit. temp. The formula of Rayleigh is not applicable. W. ALBERT NOYES, JR.

Polarization of the light scattered by mercury vapor near the resonance periodicity. LORD RAYLEIGH. *Proc. Roy. Soc. (London)* **102A**, 190-6(1922).—White light scattered at right angles by Hg vapor is completely polarized. Radiation removed by filtration appears to lie within a spectral range of about 1-100 Å. W. ALBERT NOYES, JR.

The scattering of hydrogen positive rays and the existence of a powerful field of force in the hydrogen molecule. G. P. THOMSON. *Proc. Roy. Soc. (London)* **102A**, 197-209(1922).—Positive rays of approx. 10,000 v. energy were produced in H_2 and analyzed in the ordinary way by magnetic and elec. fields. A diaphragm with a slit was used to cut out all but those desired and the rest passed through a chamber contg. H_2 as the scattering gas. Finally they were received in a Faraday chamber with a slit of variable width. The charge received by the Faraday chamber was detd. as a function of the width of the slit, when this was larger than the geometrical shadow of the slit in the diaphragm. Scattering was much larger than predicted by theory. Conclusion.—At distances of the order of 10^{-8} cm. from a nucleus there is a field of force many times stronger than ordinary electrostatic force and capable of acting on a positively charged particle.

W. ALBERT NOYES, JR.

Electric conduction across minute air gaps. JAMES W. BROXON. *Phys. Rev.* **20**, 476-85(1922).—Two optical surfaces of equal curvature were made conducting by a thin deposit of Au, the upper one being semi-transparent. Thus the distance between them could be measured by interference rings. Where the resistance was measured Ohm's law was found to hold for considerable gaps—up to several wave lengths of Na light. Conduction persisted to a wider gap when the plates were being sepd. than that at which it was resumed when they were brought together. With care to exclude dust, the surfaces could be brought to within $1/2$ -1 wave length without showing any conduction under a potential of 36 v. The proximity of radioactive material had no effect, so that the conduction seemed due to metal projections from the surfaces or to dust mostly. No disruptive discharge was obtained on nonconducting gaps even with a potential of 640,000 v./cm. The results indicate that there is no electron atm. at the surfaces as has been postulated—at least not beyond $1/4$ wave length from the surfaces. A. E. S.

Energy losses accompanying ionization and resonance in mercury vapor. J. A. ELDRIDGE. *Phys. Rev.* **20**, 456-75(1922).—The resonance and ionization potentials are measured by accelerating the electrons from an oxide-coated Pt foil, heated by radia-

tion from a W spiral, by means of a *fixed* potential. The electrons then traverse a chamber where they collide with atoms of Hg vapor whose pressure is controlled by heating a reservoir of Hg in a side tube. Some of these electrons pass through a small hole in the diaphragm sepg. this chamber from the rest of the app. In the rest of the app. the pressure of the Hg is maintained as low as possible by liquid air. The electrons after passing into the rarified part of the app. pass through another similar hole in a diaphragm into a chamber in which there is a *variable* retarding field, impeding their reception by a Faraday cylinder. The electron current to the Faraday cylinder is then measured as a function of the retarding field for various values of the initial accelerating field. Thus velocity distribution curves of the electrons after impact with Hg mols. in the high-pressure chamber are detd. By this method a crit. study is made of the various resonance and ionizing potentials obtained by previous observers. The results confirm the resonance impacts involving a loss of energy of 6.7 v. found by Foote and Mohler. They further show that the losses of this sort do not occur until the initial energy of the electrons exceeds 8.5 v., and that when the initial energy rises above the ionizing value, impacts involving a loss of energy to resonance of 6.7 v. become far more prominent than the 4.9 v. impacts. Energy losses corresponding to 5.7 v. are also found in agreement with the results of Franck and Einsporn. The method fails, however, to detect the other resonance potentials obtained by the latter observers. Finally it is found that the electron loses *all* its initial energy at ionization even though it had more than the ionizing energy to begin with. The electron emitted in such an ionizing impact also possesses no energy. This result seems to be in contradiction with the Bohr theory.

LEONARD B. LOEB

The sparking potential of a gas. G. HOLST and E. OSTERHUIS. *Compt. rend.* 175, 577-80 (1922).—H. and O. state that according to Townsend's theory of ionization by collision the sparking potential of a gas is independent of the material of which the electrodes are made. From expts. on the min. sparking potentials in the inert gases they find that the *nature of the cathode* is of considerable importance. This leads to a new theory of sparking. According to this theory the $+$ ions do not form ions by collision with gas mols., but liberate electrons from the cathode by "electrostatic attractions." The probability W of a $+$ ion liberating an electron from the cathode is found to be a function of Richardson's thermionic const. Φ , which is a characteristic of the metal. Sparking will then occur when the potential between the electrodes is such that the product of the no. of $+$ ions formed by one electron in crossing the plates, and the probability W is > 1 . When this condition holds the current becomes self-maintaining owing to liberation of electrons from the cathode and the spark can pass. In inert gases where the electron impacts are assumed perfectly elastic the no. of $+$ ions formed depends on g the no. of times that an electron starting from the cathode can liberate another electron by impact with gas mols. H. and O. det. g for Mg and for the alkali metals exptly. at the min. sparking potential and thus obtain W to be $1/a_0$ for the former, and $1/15$ for the latter. Once W is known it is possible to est. the quantity of g required for sparking in any gas. The sparking potential can then be computed for any pressure or distance between the electrodes if the ionization potential of the inert gas be known, for the sparking potential = g multiplied by the potential necessary for an electron in the gas at a pressure p and plate distance a to cause it to ionize. This potential is greater than the ionizing potential and may be computed by an equation of Hertz from the ionizing potential for any pressure. On the basis of this theory H. and O. compute a family of ionization potential curves for Ne as a function of pressure times plate distance for different values of g (*i. e.*, applicable to different cathodes). It is claimed that these curves agree in a satisfactory manner with the observed curves. In gases where the impacts of electrons with mols. are less elastic this theory ceases to hold and the effect

of the electrodes vanishes. It is for this reason H. and O. claim that the influence of the cathode has hitherto been considered negligible. [This very interesting theory depends on the assumption that W is a function of Richardson's const. only, and that it is independent of the energy of the $+$ ion when it strikes the cathode. It seems to the abstractor that the independence of W and the energy of the ion must be proved exply. before the theory can be accepted. Abstractor's note.]

L. B. LOEB

A new method for studying ionizing potentials. H. D. SMYTH. *Proc. Roy. Soc. (London)* 102A, 283-93(1922).—A new method for detg. ionizing potentials is described. The ions are produced in the gas by the impact of slow electrons of known energy. The electrons come from a W filament, are accelerated by a small elec. field V_1 and then retarded by an equal field V_2 . The mols. to be ionized stream perpendicularly across this second elec. field between two gauzes. Between these gauzes the electrons collide with the mols. at velocities between V_1 and 0. The field V_2 prevents the electrons from going beyond the second gauze and also extracts any positive ions from between the two gauzes. These positive ions are then further accelerated by a third elec. field V_3 until they reach the first of the two slits by which a beam of ions is defined. This beam is then studied by the method of positive ray analysis. The method has been applied to the study of Hg vapor. The preliminary results indicate that doubly charged Hg ions are formed at 19 ± 2 v. A consideration of the enhanced spectrum of Zn and Cd in connection with this result, indicates that the double ions formed at this voltage are the results of two impacts. At high voltages double ions may be formed by single impacts. The more highly charged ions were present in such small quantities that their identification was uncertain even at voltages as high as 500.

A. W. SMITH

Speculation concerning the positive electron. OLIVER LODGE. *Nature* 110, 696-7(1922).—L. suspects the existence of ultimate units or "negative and positive electrons" consisting of "concd. locked right-handed and left-handed screw twists in the ether, simultaneously and inevitably produced and connected with each other by transferable lines of force." These combine in great numbers to form protons, and other nuclei. For details, the original should be read.

NORRIS F. HALL

The ionizing potential of positive ions. J. S. TOWNSEND. *Phil. Mag.* 44, 1147-8 (1922).—A note replying to Saxton (*C. A.* 17, 22) showing that it is not the mean free path in H_2 that det. ionization by positive ions but it is the number of ions which through probability attain paths sufficiently long to produce ionization by collision. Calens. from expts. at 8 mm. pressure show the ionization potential must be about 10 v., while those at lower pressure show it must be above 15 v.

S. C. L.

The ionization potential of abnormal helium atoms by low-voltage electronic bombardment. FRANK HORTON AND ANNE C. DAVIES. *Phil. Mag.* 44, 1140-6(1922).—The discovery of Kannenstine (*C. A.* 16, 2634) that with a c. exceeding 220 alternations per sec. an arc may be struck in He at about 5 v. has led H. and D. to a new examn. of the subject. They assume that the crit. low voltage is the difference between the ionization voltage (25.2 v.) and one of the 2 crit. electron energies for the production of radiation (20.4 or 21.2 v.) leading to 4.8 or 4.0 v. as the crit. difference. Direct expt. by H. and D. show a value about 4.5 v. and the explanation for the striking of the arc at this low voltage is offered that the interval elapsing between the breaking of the arc and the new application of energy was sufficiently short for the survival of a considerable no. of the abnormal atoms. The assumption of a metastable state of He made by Kannenstine is not regarded as necessary.

S. C. LIND

Scattering of X-rays by crystals. G. E. M. JAUNCEY. *Phys. Rev.* 20, 405-20 (1922).—By means of both homogeneous rays (K_α of Mo obtained by preliminary reflection from a rock salt crystal) and heterogeneous rays directly from a Mo or W target, the scattering curves for rock salt and calcite crystals, Al and glass are obtained by measuring

the ionization currents for various angles of scattering. On account of the small intensity of scattered radiation, incident beams of $15'$ to $8''$ width and a scattered beam of 6° width are required even with a sensitive Compton electrometer. For angles from 50° to 150° the curves for the crystals are of the same shape as those for Al and glass, each curve showing a min. at about 100° . For angles below 50° the crystal curves fall below the others and each shows a max. at a larger angle between 15° and 30° depending on the wave length. In addn. to the general scattering at all angles there appear for cryst. substances maxima corresponding to the Laue spots. In order to discover whether or not the intensity of radiation is dependent upon mol. orientation, a theoretical curve is derived from the formula, independent of orientation, $I_\phi = [s_\phi I_0/k] \cdot [\sin(\phi - \theta)/\sin(\phi - \theta) + \sin \theta]$, where I_ϕ is the intensity at the angle ϕ , s_ϕ the linear scattering, I_0 the energy of the primary X-rays and θ the angle of incidence. With this curve the exptl. ones coincide, except for the humps in the latter due to regular reflection. Hence scattering is independent of orientation and the atoms are apparently isotropic. Scattered radiation is always softer than the primary. The total energy scattered in all directions is an appreciable fraction (e. g., 0.7 for K_α of Mo by calcite) of the energy reflected in the 1st order spectrum line. Comparison with the Debye theory of scattering (C. A. 8, 1912; 9, 2032) shows agreement only for rock salt above 60° and the prediction that the scattering by crystals and amorphous substances should be greatly different is not verified. Approx. calcs. of the no. of electrons in the atoms are made from the scattering data.

G. L. CLARK

The effect of temperature on the scattering of X-rays by crystals. G. E. M. JAUNCEY. *Phys. Rev.* 20, 421-3(1922); cf. preceding abst.—Because of disagreement with the scattering predicted by Debye explanation is attempted from expts. on the effect of temp. With X-rays from a W-target tube operated at 95 kv. the ratio of the radiation scattered from a crystal at 295° to that for the same angle at 17° is found to be 1.33 and 1.18 for rock salt at angles of 15 and 30, resp., and 0.99 and 1.03 for calcite at 30° and 73° , resp. There is thus a marked effect for rock salt but none for calcite, which acts like an amorphous substance; but even the effect for rock salt is smaller than predicted by the Debye theory.

G. L. CLARK

The scattering of approximately homogeneous X-rays by powdered crystalline carbon, metallic lithium, and liquid benzene, mesitylene, and octane. C. W. HAWLETT. *Phys. Rev.* 20, 688-708(1922).—The scattering and absorption of homogeneous X-rays (K_α of Mo isolated with a ZrO_2 filter) in diamond and graphite, Li, and the liquids C_6H_6 , mesitylene and octane are detd. by measuring the intensity of radiation scattered by the substance placed in a small capsule at the center of the spectrometer for angles from 20° to 165° . For the first 3 the results of Hull with the photographic method are checked. Each of the liquids shows 1 max.: 8.5° for C_6H_6 , 6.5° for mesitylene and 8.1° for octane, indicating a crystal structure with planar spacings of 4.8, 6.3 and 5.0 Å., resp. For very small angles the scattering is 0 for solids and approaches 0 for the liquids. The mass-absorption coeffs. are detd. by integrating the area under the above mentioned curves or exptly. integrating the ionization currents for all angles of scattering. The coeffs., 200 for C and 0.168 for Li agree, with Thomson's theoretical values; for the liquids the values 0.238, 0.244 and 0.262, resp., are 10% larger than predicted by theory. The true mass-absorption coeffs. calcd. from the total scattering and the density are in accord with $KN^3\lambda^3$, where the mean value of K is 4.38×10^{-3} and N is the at. no. Full exptl. details are given for detg. the ratio between the flux of radiation into the ionization chamber and the flux of the energy falling on the scattering material by means of a rotating Pb disk. The mass scattering coeffs. for at. C and H are 0.220 and 0.463, resp., both larger than theoretical values.

G. L. CLARK

Experiments on X-ray series. ELIS HJALMAR. *Compt. rend.* 175, 878-80(1922);

cf. *C. A.* 16, 2259.—The M-series wave lengths for elements W(74) to U(92) are detd. and tabulated. While previous work has indicated only 3 principal members of the series, there are in reality 24 for U including satellites ranging from $M_{\alpha}P_1$ (indicating energy level origin) 2.248 to $M_{\beta}N_3$ 4.929 Å. The M-O series rays are controlled by a principle of selection of 1 unit change in the quantum no., or $n \rightleftharpoons n+1$, while the M-N series follow the rule $n \rightleftharpoons \begin{cases} n \\ n+1 \end{cases}$. The O energy level contains 5 rings.

G. L. CLARK

An experimental determination of the true absorption coefficients of hard X-rays. W. STATZ. *Z. Physik* 11, 304-25(1922).—An extensive crit. survey of all work on absorption of X-rays, notably that of Barkla, Hull, Richtmyer, Hewlett, Holthusen and von Auren, is made in the beginning. The usual absorption formula is $I = I_0 e^{-\mu d}$, where I is the intensity observed, I_0 the energy of the primary beam, d the thickness, and $g = \mu + s$, where μ is the true absorption coeff. and s the scattering coeff. Of the 3 ways to sep. the factors in g , S. prefers to measure g and μ , and find s by difference. The values of μ for Al and H_2O are obtained by using hollow spherical absorbers (the H_2O in celluloid) and measuring the intensity at the center of the sphere by a special very small ionization chamber. For the short wave lengths used (0.1 to 0.5 Å.) the curves of $\log \mu/p$ against $\log \lambda$ are straight lines practically coinciding with curves from values extrapolated from longer wave lengths. Utilizing the work of Neukirch on γ -rays for further extrapolation, a considerable deviation in the behavior points to a selective absorption under $\lambda = 0.1$.

G. L. CLARK

Extraordinary diffraction of X-rays. L. W. MCKREHAN. *J. Optical Soc. Am.* 6, 989-97(1922).—The directed emission of characteristic X-rays from the atoms of a crystal placed in a narrow beam of X-rays contg. sufficiently short wave lengths is theoretically analyzed. Six assumptions are necessary to enable building upon the elementary theory that appreciable energy in the form of secondary waves will be emitted only in those directions along which at great distances the secondary waves from all points in the space lattice agree in phase. In ordinary diffraction incident and diffracted wave lengths are equal, or $\lambda_1 = \lambda_2$, while in extraordinary diffraction $\lambda_1 < \lambda'_2 < \lambda_2$, where λ'_2 is the crit. absorption wave length. The extraordinary ray as geometrically considered should deviate less from the transmitted ray than the ordinary. Laue photographs should show additional spots due to single characteristic wave lengths from the atoms in the crystal. The only exptl. evidence aside from certain anomalies observed on photographs is the existence of both ordinary and extraordinary diffraction from KI crystals observed by Clark and Duane (*C. A.* 16, 4134). The existence of extraordinary diffraction thus seems to favor the existence of spatially limited energy quanta in the incident beam and also of cyclic motions within the atoms which cause occasional recurrences of configurations unstable when coincident in time with the presence of a passing quantum of energy. [Unfortunately the conclusions are entirely inconsistent with the geometrical conception of interference as developed. **ABSTR.**] G. L. C.

A balance method of measuring X-rays. S. RUSS AND L. H. CLARK. *Phil. Mag.* 44, 1159-64(1922).—A balance method based on that of Bronson (*Phil. Mag.* [6] 11, 143(1906)) is described. Two ionization chambers are electrically connected and one of them is exposed to X-radiation, the other to γ -radiation from a known source of Ra. Balance is indicated by the attainment of a steady deflection of the leaf placed in one of the chambers, but also joined metallically to an electrode in the other one, under a const. potential from a battery set. This method permits of expressing the intensity of X-radiation in terms of γ -radiation, but only after the arbitrary specification of the governing factors in the two cases, such as distance, screening etc. The desirability is expressed of an international agreement on these specifications, which will enable one to express X-radiation in terms of γ -radiation without misunderstanding. S. C. L.

The X-ray structure of potassium cyanide. P. A. COOPER. *Nature* **110**, 544 (1922); cf. *C. A.* **16**, 3427.—Bozorth's structure of the KCN mol. (cf. *C. A.* **16**, 1523) is based on the assumption that the relative intensities of the spectra would decrease in a normal manner if the structure were like NaCl. He gave no nos. for the observed intensities, but gave 100 : 10 : 3 as the relative values of the (100), (200) and (300) reflections required to satisfy his particular structure. Measurements by C. gave 16–17 as the relative value for the (200) reflection, corresponding to 20 for NaCl. The fact that KCN has a lower m. p. than NaCl suggests that even at ordinary temps. the heat vibrations are of unusual amplitude, and this explains why the intensities of the spectra decrease more rapidly than normally. The probable electron distribution in a composite CN radical is another important factor causing the normal sequence to decrease rapidly. C. C. DAVIS

Variation of the intensity of reflected X-radiation with the temperature of the crystal. IVOR BACKHURST. *Proc. Roy. Soc. (London)* **102A**, 340–53 (1922).—The theories of Darwin and Debye for the effect of temp. on X-ray reflection show that the intensity of reflection decreases as the temp. of the crystal increases and that this decrease is the more rapid as the angle of reflection is increased. These conclusions are supported by the expts. of Bragg and by the expts. described here except in the case of the sapphire and ruby. The method was that adopted by Bragg with modifications to admit of a higher range of temps. and greater accuracy in measuring the temp. of the crystal. Al was studied at temps. between 50° and 500° for the K-radiation from Mo. A very marked decrease in intensity was observed with rise in temp. and fair agreement with the theory of Debye for the (100) and (222) spectra. In the case of carborundum and the other substances studied the temp. was extended to 900°. The decrease in the intensity with rise of temp. was much greater for the higher-order spectra. The K_{α} - and the K_{β} -radiations gave different curves for the (333) spectra. In graphite a definite temp.-intensity curve was obtained only for reflection from the cleavage plane. For the K_{α} -radiation from Mo there is a decrease in the intensity of radiation with rising temp. In diamond no change of intensity for any of the spectra investigated could be measured with certainty. In ruby and sapphire the decrease of the intensity of the spectra (111) was greater than that of (222). This anomaly can be explained by assuming that the atoms of the Al pair remain in contact and do not take part in the expansion of the lattice. A. W. SMITH

Activation of contact platinum by Röntgen rays. R. SCHWARZ AND M. KLINGENFUSS. *Z. Elektrochem.* **28**, 472–3 (1922).—Pt used as contact agent in the oxidation of SO_2 to SO_3 was subjected to the action of X-rays, in the presence of a current of moist air, for a period of 2 hrs. At 400° the yield of SO_3 was increased from 94.6 to 95.9% when the activated instead of ordinary Pt was employed as contact agent. At 260° the yield was increased from 35 to 51% SO_3 . The change brought about in the Pt by the action of X-rays is not permanent. At the end of 24 hrs. the Pt has completely lost its activity. H. JERMAIN CREIGHTON

Quantitative investigations of the line spectra of vanadium in fused salts. A. DE GRAMONT. *Compt. rend.* **175**, 1129–33 (1922).—Complete tables give the results of a quant. study of the spectral lines of V, indicating the successive disappearance of the various lines with decreasing concn. of the source (V_2O_5 dissolved in purified Na_2CO_3). The app. and method are similar to those employed by de G. in a study of various other elements (*C. A.* **12**, 1358; **14**, 2510; **15**, 811, 3587) for use in quant. chem. analysis and in mineralogy. R. T. BIRGE

The law of dispersion of prismatic spectra in the ultra-violet. PIERRE SALET. *Compt. rend.* **175**, 1141–3 (1922).—The simple formula for the dispersion on prismatic spectra previously suggested by S. (*Compt. rend.* **160**, 715 (1915)) is here applied to the

ultra-violet, and between the limits $\lambda 2250$ and $\lambda 3100$ is found to give an agreement with the observations within the limits of exptl. error. The proper method for using the formula with various types of dispersion is indicated briefly.

R. T. BIRGE

Excitation of the spectra of mercury, influence of helium. GEORGES DÉJARDIN. *Compt. rend.* 175, 952-5(1922).—The conditions for exciting the spectra of Hg are sought by analyzing, with a spectrograph, the light emitted by Hg vapor traversed by electrons with variable velocity. A 3-electrode tube is used in which the cathode is an incandescent W filament, and the grid and plate are connected to form the anode. A p. d. increasing progressively from 0 to 100 v. is applied and the region between the electrodes is projected with a lens on to the slit of a spectrograph. The arc spectrum appears when the electron velocities exceed that corresponding to the ionization potential of 10.4 v., but certain of these spectral lines change in relative intensity at higher voltages. The spark lines are produced by high-speed electrons and indications are obtained for several groups of rays of different character but their excitation potentials were not accurately detd. In the presence of He only the arc spectrum of Hg is observed below 20.4 v., which is the first crit. potential for He. Electrons with greater speeds, however, produce rather intricate changes in the relative intensities of arc and especially of spark lines, when He is mixed with Hg vapor.

W. F. MEGGERS

Series relations in the arc spectrum of chromium. H. GIESELER. *Ann. Physik* 69, 147-60(1922).—Measurements of the Zeeman effect on spectral lines of Cr made it possible, with the help of Landé's theory (*C. A.* 15, 3587), to arrange groups of lines and indicate their series relations. The $3a/2$ magnetic seps. gave the key to the Cr spectrum. Three groups of 12 lines each were found. These lie between the wave lengths 3883-3941, 2967-3005 and 2871-2911 Å. and are designated as combinations of a 5 fold p term with quintuple p' , p'' and p''' terms, resp. Similarly, 2 groups in the wave-length intervals 4337-4412 and 3014-3037 Å. are recognized as pd^1 combinations. Three groups, 4497-4652, 2988-3053, 2726-2780 Å., are ascribed to a pd^1 series in which the d^1 term is only 3-fold, but there are 6 p -terms. Similarly a ps group is indicated between 5204 and 5410 Å. where the s term is triple and the p -term 6-fold. A table of observed and computed magnetic resolutions for 34 Cr lines concludes the paper.

W. F. MEGGERS

Selective absorption of electric waves in dielectrics. V. ROMANOV. *Ann. Physik* 69, 125-46(1922).—The emission and absorption spectra of substances furnish a means of investigating the structure of mols. and atoms. The optical part of the spectrum has been most carefully studied; many data also exist for the adjacent ultra-violet and infra-red portions, but little is known of the elec. part of the spectrum. A new method of investigating the selective absorption of elec. waves is described. Elec. waves from 57 to 88 cm. in length were generated and propagated along parallel wires between which a few drops of a liquid dielectric were placed. A thermoclement inserted in the liquid measured the heating of the liquid caused by absorption of the elec. waves. A 2nd thermoclement measured the energy of the resonator waves and the ratio of the 2 readings gave a measure of the absorption in the dielectric. In this way the absorption of elec. waves was investigated for 5 alcs. (MeOH, EtOH, PrOH, iso-Bu alc., and AmOH). Selective absorption was found in all of these, max. absorption occurring for wave length of about 57 cm. and decreasing with longer waves. The app. described did not permit absorption measurements for waves shorter than 57 cm.

W. F. MEGGERS

Dispersion of air and of its principal constituents in the spectral interval 4388-9224 Å. EUGEN STOLL. *Ann. Physik* 69, 81-111(1922).—By means of a Jamin interferometer measurements on the n of air were made for 24 wave lengths from 4388 Å. in the violet to 9224 Å. in the infra-red. The values found for pure out-door air are closely represented by the interpolation formula $(n_0 - 1)10^7 = 2871.87 + 16.170/\lambda^2(\lambda$

in μ). Similar measurements were made on the n of O_2 , N_2 and CO_2 , and the values are well represented by the following 2-term Cauchy dispersion formulas: $(n_0 - 1) \cdot 10^7 = 2650.86 + 20.074/\lambda^2$, $(n_0 - 1) \cdot 10^7 = 2977.27 + 22.65/\lambda^2$ and $(n_0 - 1) \cdot 10^7 = 4406.97 + 29.584/\lambda^2$. The exptl. results give $(n_0 - 1)$ correct to about 0.02% in abs. value and about 0.01% in relative value.

W. F. MEGGERS

The structure of the red lithium line. T. R. MERTON. *Nature* 110, 632(1922).—McLennan and Ainslie (*C. A.* 16, 3253) announced the discovery of a new component of the line λ 6708 in the spectrum of Li, the line appearing as a quartet. They suggested that this structure is due to 2 pairs of lines, each pair being assigned to one of the isotopes of Li. To M. it appears that the new components cannot be accounted for in this manner. The line is usually observed as a single pair, with higher vapor pressure a third component appears and with a still greater amt. of vapor reversal gives what appears to be a quartet. The relative intensities of the components are not in accord with the view that they are due to the 2 isotopes and the observed sepn. are between 3 and 4 times greater than that calcd. from Bohr's theory.

W. F. MEGGERS

The spectrum of neutral helium. C. V. RAMAN. *Nature* 110, 700-1(1922).—Silberstein (*C. A.* 17, 364) proposed a new combination principle to explain the spectrum of neutral He. A careful survey of the figures has brought R. to the conclusion that the approx. agreements between the calcd. and actual frequencies are merely fortuitous arithmetical coincidences.

W. F. MEGGERS

Effect of certain dissolved substances on the infra-red absorption of water. J. R. COLLINS. *Phys. Rev.* 20, 486-98(1922).—Infra-red absorption spectra of aq. solns. of 16 inorg. compds. from 0.8 to 2.3μ have been detd. to see how the dissolved substances affect the absorption of the water. Readings were taken alternately with a cell contg. a soln. and with one contg. water. Curves were thus obtained for the alkali hydroxides, 5 chlorides (Al, Ca, Mg, Na, Sr) 5 nitrates (Ag, Al, Mg, NH_4 , Zn) and 3 sulfates (Ag, Na, Zn). All solutes decreased the absorption in the water band at 1.44μ and probably also in the band at 2μ , whereas all excepting $Al_2(SO_4)_3$, $ZnSO_4$ and the hydroxides increased the absorption in the bands at 0.97 and 1.2μ . These results do not agree with the solvate theory which ascribes the effect to the formation of hydrates, since some non-hydrating compds. decreased the absorption at 1.44μ . Absorption of water, from 0.8 to 2.3μ , was measured by using cells of different known thicknesses. The wave lengths of max. absorption were found to be 0.97, 1.20, 1.44, and 2.00μ , and the corresponding coeffs. came out 0.448, 1.220, 29.4, and 103, resp. Such difference as there is between these results and those previously obtained may be due to elimination of stray light. The fact that in the absorption spectrum of water vapor the bands at 1.44 and 2μ are stronger and the other two bands weaker than for liquid water suggests that the former two bands are associated with a different kind of mol. than the latter two bands. If so, the effect of a dissolved substance on absorption may be due to a change in the relative number of these kinds of mols. produced by the presence of the substance.

W. F. M.

Absorption coefficients for homogeneous X-rays. E. G. TAYLOR. *Phys. Rev.* 20, 709-14(1922).—By means of a spectrometer with various Pb slits and a calcite crystal the K_α of Mo was reflected into the ionization chamber and the effect of interposing a cell contg. a known thickness of liquid observed. The liquids used and the absorption coeffs. $\times 10^{24}$ are as follows: pinene $C_{10}H_{16}$ 1.209; limonene $C_{10}H_{16}$ 1.206; benzene 0.707; toluene 0.834; isopropyl alc. 63.8; Me propionate 108.9; Et acetate 109.9; acetone 67.9; Et formate 97.0; trimethyl glycol 98.6. From these values the at. absorption coeffs. for C, H and O may be computed, assuming absorption an additive property: 11.00 to 11.55×10^{-24} for C; 0.45 to 0.50×10^{-24} for H, and 29.9 to 31.0×10^{-24} for O. The computed coeffs. are within $1/4\%$ of the observed, except that acetone and H_2O are 1% too low.

G. L. CLARK

Arc spectra and ionization potentials in dissociated gases. K. T. COMPTON. *Proc. Am. Phil. Soc.* 61, 212–26 (1922).—The arc was studied in a new type of discharge tube the wall of which was a cylinder of W foil that could be heated by elec. current. The discharge passed from this wall to an axial W wire, also heated. The gas pressure ranged from 0.5 to 5.0 mm. This device permitted the use of an atm. of at. H. Crit. potentials were also studied by a modification of the Lenard method. A hot W grid furnished H atoms, and means were provided for observing the effects of radiation and ionization separately. For H six crit. potentials were observed; 10.1, 12.1 and 13.8 are associated with the atom, the first two being radiation potentials, and the last the ionization potential. These values correspond resp. to the 1st and 2nd lines and the convergence frequency of the Lyman series. The values 11.3, 12.8 and 16.2 refer to the mol., being due, resp., to ionization without dissociation, dissociation plus radiation from an atom, and dissociation plus ionization of an atom. The lowest voltage at which an arc can be maintained in H is 16.2 v. A similar study of N showed the arcing voltage to be 16.15 v., at which value the positive bands were observed. One of these increased in intensity with further increase of voltage, the second decreased. The negative band appeared at a voltage somewhat higher than 18 v. and increased in strength with the voltage. The lines in the visible region of the spectrum were not seen at a potential below 70 v. While no dissociation of N was possible at temps. obtained by the heated tube, dissociation by electronic bombardment was facilitated by the hot W. K. B.

The electric-furnace spectrum of iron in the ultra-violet, with supplementary data for the blue and violet. A. S. KING. *Astrophys. J.* 56, 318–39 (1922).—While furnace emission spectra extend into the ultra-violet only so far as the continuous spectrum of a black body at the same temp. may be observed, it is now shown that a sufficiently hot back-ground source shows the absorption spectra of the vapor at high or low temp. extending beyond λ 2300 Å. At the same temp., the relative intensities of the lines are the same in emission and absorption (when present as emission). Tables give the temp. classification of 904 lines, λ 2298 to 3878 Å., and the relative intensities in the arc and in high-, medium-, and low-temp. furnace spectra, upon which the classification is based. For Fe, the low-, medium- and high temp. lines are well developed at 1800°, 2000°, and 2300°, resp. Some 60 lines are relatively very weak in the arc; these are denoted as Class IA, IIA, etc. The most persistent low-temp. lines are illustrated by the 21 which occur between λ 3745 and 4531 Å. emitted by vapor at 1400°. A revised classification of 262 lines, λ 3884–4531 Å. (C. A. 7, 1838), is based on recent spectrograms. A study of various metals shows a parallelism between temp. classification and the crit. potentials of the low-voltage vacuum arc. For high-boiling metals, crit. voltage data may perhaps be more readily detd. from furnace observations than from direct observation, once the 2 methods have been correlated by means of those elements which can readily be observed in either way. K. BURNS

Researches on the luminescence of gas in the electrodeless discharge. The induction spectrum of cesium and rubidium. L. DUNOYER. *J. phys. radium* 3, 261–92 (1922); cf. C. A. 16, 20.—A luminescent discharge is induced in a tube, surrounded by a coil of wire through which is passing a high-frequency oscillatory current. In this way, electrodes inside the tube are eliminated. A review of work on this type of discharge is given. Complete spectra of Cs vapor and Rb vapor are given. They are compared with spectra obtained in the Geissler tube, in the flame and in the arc. Since slight changes in temp. make an appreciable difference in the spectrum, the temp. of the whole discharge chamber is regulated by means of a thermostat. The measurements range from 100° to 300°. The application of these spectra to the structure of the atom is discussed. F. D.

The phosphorescence of magnesium sulfide activated with rare-earth metals.

Experimental studies. ERICH TIEDE AND ARTHUR SCHLEEDT. *Ann. Physik* **67**, 573-80(1922).—MgS was prepd. by heating MgSO_4 to 900° in a current of N satd. with CS_2 . Rare earths of the Ce and Yt groups were added in a concn. of 1:1000. The emission spectra in the visible, when excited with ultra-violet light and with cathode rays were studied. Several spectra are reproduced. The spectra are quite different with the different rare-earth metals.

FARRINGTON DANIELS

A study of the exciting power for fluorescence of the different parts of the ultra-violet spectrum. L. J. BOARDMAN. *Phys. Rev.* **20**, 552-72(1922).—About 70 substances were exposed to different regions of the spectrum extending from 0.55 to 0.20μ to det. what wave lengths are effective in exciting fluorescence, and what relations exist between the exciting wave lengths and the corresponding absorption and fluorescence spectra. A preliminary study, visually, revealed no excitation for 20 oxides and 8 chlorides; a few silicates, phosphates and sulfates fluoresced faintly; some like anthracene, eosin, etc., fluoresced well, while 20 uranyl compds. fluoresced strongly. The exciting wave lengths for the uranyl compds. extend from 0.55μ to 0.35μ . The fluorescence spectra of 12 uranyl compds. were then photographed and measured on a spectrophotometer and the data derived show that every excitation band observed corresponds to an absorption band of the compd. This fact permits the extension of the absorption spectrum into both the red and violet spectral regions.

C. C. KIESS

Spectra of hydrogen, nitrogen and oxygen in the extreme ultra-violet. J. J. HOPFIELD. *Phys. Rev.* **20**, 573-88(1922).—By means of a vacuum grating spectrograph and special photographic films, directions for the prepn. of which are given, exposures were made to the spectra emitted by H, N and O. The light source was an oil-cooled pyrex tube through which a continuous flow of gas at low pressure could be maintained. In general the exposures required to secure good spectrograms were only a few min. Measurement of the films yielded the following wave-length data: for H, 90 lines between 885 \AA . and 1059 \AA .; for N, d. c., about 30 lines and bands between 1025 and 1745 \AA .; for N, disruptive discharge, 80 lines between 834 and 1751 \AA .; for O, about 100 lines between 507 and 1299 \AA . When Hg vapor was mixed with O, about 15 new lines between 433 and 788 \AA . were observed. Many of the lines observed by Lyman in the spectrum of He agree in wave length with H's N and O lines. Light was transmitted to the grating when the pressure within the spectrograph was as high as 3 cm . Hence both O and N possess, in the regions examd., a high degree of transparency and are not opaque as is commonly supposed.

C. C. KIESS

The ultra-violet absorption spectra of pyridine and of isoquinoline. H. FISCHER AND P. STEINER. *Compt. rend.* **175**, 882-4(1922).—Sols. in hexane, ether and alc. of pyridine and isoquinoline, and also sols. in CCl_4 and H_2O of pyridine were examd. spectroscopically and were found to possess characteristic absorption spectra in the ultra-violet. For pyridine 6 bands were measured, and 10 bands for isoquinoline. The absorption curves of the 2 compds. agree in general in showing a series of narrow bands on the side of longer wave lengths followed by a broad one farther to the violet and by very intense bands in the extreme ultra-violet. The curve for isoquinoline is displaced approx. 100 \AA . to the red from that for pyridine. The curves and tables presented give wave length and intensity data for the observed bands.

C. C. KIESS

The ultra-violet absorption spectra of toluene and some xylenes. F. W. KLINGSTEDT. *Compt. rend.* **175**, 1065-7(1922).—A soln. of toluene in hexane has 16 absorption bands between 2685 and 2424 \AA . These bands may be distributed among 4 groups in which the intensity of each band decreases with wave length, and between the members of which const. frequency differences exist. The absorption spectrum of *o*-xylene has 3 broad bands, that of *m*-xylene has 5 bands, and that of *p*-xylene has 12 narrow bands, which may be distributed in 3 groups characterized by const. frequency differ-

ences, and diminishing intensity with decreasing wave length. From the graph given the wave lengths and intensities of the bands may be read. C. C. KIESS

The intensity of multiple lines and their Zeeman components. A. SOMMERFELD AND W. HEISENBERG. *Z. Physik* 11, 131-54(1922).—The correspondence principle permits estimates to be made of the intensities of spectral lines from the kinematical character of the at. orbits. A mathematical analysis of the motion of the series electron leads to expressions for the intensities of multiple lines and their Zeeman components. A comparison of the intensities thus derived with those actually observed in the doublets of the alkalis, the triplets of the alk. earths, the multiplets of Cr or Mn, and the components of lines resolved in a magnetic field affords verification of the theory.

C. C. KIESS

New spectra of water vapor, air and hydrogen in the extreme ultra-violet. J. J. HOPFIELD. *Nature* 110, 732-3(1922); cf. *C. A.* 16, 685; Wood, *C. A.* 16, 4136.—Water vapor gives a spectrum in the ultra-violet extending to about 900 Å. consisting of O₂ lines, H₂ series lines, the secondary spectrum of H₂ and certain other lines probably not due to H₂. By using a condensed discharge at low pressure of air a spectrum was obtained for air to 350 Å. Many He lines about 600 Å. were found on the plate. Wet H₂ and a long discharge tube gave 3 new lines of the Lyman series. On many films there was a line at 243 Å., agreeing with the equiv. wave length for the I. crit. potential of O₂. This indicates that the great absorption band of H₂ which begins at about 850 Å., terminates on the long wave length side of 243 Å., and as it appears in the case of H₂ at a pressure of 0.3 mm. after the light passes through a distance of 1 m. it shows the transparency of H₂ in this region.

A. E. STEARN

The measurement of light. J. W. T. WELSH. *Phil. Mag.* 44, 1165-8(1922).—A discussion as to the logical fundamental unit in photometry, whether one of brightness or of illumination. The conclusions are: (1) The fundamental photometric magnitude from the point of view of visual measurement is brightness not illumination. (2) The photometric unit is one of luminous intensity (c. p.) or luminous flux. (3) Of the two possible systems of definition based on these resp. magnitudes, that based on the magnitude in which the unit is maintained seems preferable, because it follows the natural order of mental conception. (4) The relation between the flux unit of brightness (the lambert) and the intensity unit (c. p. per sq. cm.) is pointed out. S. C. L.

Photochemistry of chlorine detonating gas. F. WEIGERT AND K. KELLERMANN. *Z. Elektrochem.* 28, 456-8(1922).—A brief presentation of the results of an investigation of the union of H and Cl during the early stages of combination. By means of photographs of the illuminated gas mixt., it has been found that union of the gases does not take place instantly, but only after 0.01 to 0.05 sec. from the moment of excitation. The observations indicate that the combination of the components of Cl detonating gas in liquid is not a direct light-action, but a photochem. secondary effect. Details of the investigation are to be published shortly. H. JERMAIN CREIGHTON

Photochemistry of chlorine detonating gas. F. WEIGERT AND K. KELLERMANN. *Sitz. preuss. Akad. Wiss.* 24, 315-20(1922); cf. preceding abstract. D. C. B.

The photochemical formation of phosgene. MAX BODENSTEIN. *Rec. trav. chim.* 41, 585-91(1922).—A parallelopiped-shaped vessel in a thermostat at 20° was used and illuminated by a Nitra-lamp. The reaction was followed with a quartz-glass manometer. The Cl contained 0.08% O₂ and a trace of H₂O. CO from H₂SO₄ + HCO₂H was freed from O₂, CO₂ and H₂O in a large C-filament lamp over solid KOH. The results with various mixts. of Cl₂ and CO are extremely complicated and fall between 2 equations $dx/dt = k_1[Cl_2].[CO]$ and $dx/dt = k_2[Cl_2]^2.[CO]$. At the beginning the data followed the 2nd equation and this was subsequently found to be due in part to moisture present (about 0.2 mm.). The other factors were not detd. A few expts. on the re-

lation between the amt. of light absorbed to the amt. of material transformed were made. O_2 retards the reaction and exercises a rather const. effect throughout the reaction until just at the end when its effect is suddenly diminished. This is due to CO formation. O_2 is sensitized by the illuminated Cl_2 . Additional expts. showed that the CO_2 formation is, other things being equal, proportional to the CO pressure, increases with the Cl_2 pressure, but more slowly than directly proportionally to it, and decreases with increasing O_2 concn. but not so rapidly as to be inversely proportional to it. The sensitized reaction also shows a large Draper effect (in which the pressure increases at first before diminishing). A theory of this complicated reaction cannot as yet be given. E. J. W.

The development of normal and selective photoelectricity since 1914. GEBHARD WIEDMANN. *Jahrb. Radioakt. Elektronik* 19, 112-41 (1922).—A review with bibliography. J. A. ALMQUIST

Small high-intensity mercury arc in quartz glass (BUTTOLPH) 1.

KAYE, G. W. C.: The Practical Application of X-Rays. London: Chapman & Hall, Ltd. 10s. 6d. Reviewed in *J. Roy. Soc. Arts* 70, 876 (1922).

Treating radium-bearing ores. W. F. BLECHER. U. S. 1,438,357, Dec. 12. Ore which may contain V, U and Ra is comminuted and heated with H_2O and about 50% of Na_2CO_3 and after sepn. of the alk. soln. thus formed the residue is treated with an acid such as 16° B \acute{e} . HCl and the acid ext. is filtered off and treated to recover Ra.

4—ELECTROCHEMISTRY

COLIN G. FINK

Frederick Gardner Cottrell. ANON. *Elec. World* 81, 141 (1923).—Biography with portrait. C. G. F.

Electrochemistry and electrometallurgy in 1922. R. PITAVAL. *J. four Electrique* 32, 1-3 (1923). C. G. F.

Bibliography on the electrothermic metallurgy of zinc. B. M. O'HARRA. School of Mines and Mct., Univ. of Missouri, *Bull.* Vol. 6, No. 2, 65 pp. (1922). E. J. C.

High-temperature melting. ANON. *Iron Age* 110, 1507 (1922).—A description of the elec. furnace equipment of the rare metal alloy refining and melting plant of the Barro Metals Corp. The equipment includes 3 graphite resistance furnaces and 1 high-frequency induction furnace. LOUIS JORDAN

Layout for electric tool steel plant. M. W. CARUTHERS. *Iron Age* 110, 1363-4 (1922).—The importance of covered sheds for steel scrap storage is emphasized. It is the condition of the scrap, with regard to corrosion when charged into the furnace, which det. the amt. of refining necessary, the quality of the steel produced, and the life of the furnace refractories. Electrodes should be protected from exposure as excessive breakage results from the effect of moisture or frost. Details of efficient arrangement of melting platform, design of furnace pit, and the storage of refractories, ferro-alloys, and ingots are considered. LOUIS JORDAN

A molybdenum resistance vacuum furnace. P. FLEURY. *Compt. rend.* 175, 880-2 (1922).—Molybdenum wire is wound on an alundum core and surrounded by alundum. This is sealed in a vacuum iron case. The furnace can be used to 1700°. A. H. DICK

Ajax-Wyatt furnace in the brass-mill casting shop. R. P. HEUER. *J. Ind. Eng. Chem.* 14, 1021-4 (1922).—A method is developed for calcg. the proportions of a vertical ring induction furnace which will result in a well balanced mechanism. Operating

procedure and furnace schedules are discussed and a comparison is made between induction furnace and crucible melting of brass in rolling mills. LOUIS JORDAN

A new induction furnace. J. M. WEED. *Trans. Am. Electrochem. Soc.* **42** (preprint); *Chem. Met. Eng.* **27**, 977-9(1922).—A description of a new type of induction furnace for melting non-ferrous metals (see *C. A.* **16**, 3814). An explanation is given of the manner in which the magnetic forces establish max. and min. fluid pressures at opposite ends of the secondary cylinder and maintain a unidirectional circulation of metal.

LOUIS JORDAN

The manufacture of aluminium in Russia. S. D. CHÉINE. *Communications travaux tech. sci. effectués République Russe* **5**, 71-3(1921); *Rev. métal.* **19**, 568-9(Abs.) (1922).—B. J. Zbarsky has worked out a method for the com. sepn. of Fe salts from a soln. of $\text{Al}_2(\text{SO}_4)_3$, which allows of working kaolins by the so-called acid process for the production of Al. Kouznietsoff and E. J. Joukovsky treat a mixt. of Al ore, baryta (or BaCO_3) and Fe scrap in an elec. furnace, obtaining products such as ferro-Si and Ba aluminate (the latter in the form of a slag). The Ba aluminate is dissolved in water, and the Al is prepd. by one of the usual methods and the recovered Ba is re-used. This process is suitable for the Tikhvine bauxites, which contain large amts. of SiO_2 and of Fe and which could supply the whole Russian requirements of ferro-Si. A. P.-C.

The electro-preparation of solid alkali amalgams in quantity. PAUL M. GIESY AND JAMES R. WITHROW. *Ind. Eng. Chem.* **15**, 57-60(1923).—By simplifying the methods and app. of Arlt, Nernst, Kerp, and Böttger for the prepn. of solid alkali amalgams, greatly improved yields were obtained. Kerp's method is improved by having the Hg in the bottom of the cell as well as that in the jet receive current, and by using a single jet-tube with a stopcock. A pure product is obtained without an atm. of H. The method of Smith and Bennett is improved by forcing the current and by cooling the electrolyte. Shepherd's method would be best if there could be found a diaphragm unacted upon by caustic alkali and by the amalgams themselves, which offers little resistance to the conduction of the current by the electrolyte and is itself a nonconductor. Solid alkali amalgams, contrary to Kerp, are all lighter than Hg. W. H. BOYNTON

Electrodeposition of cadmium versus zinc. CHARLES H. PROCTOR. *Metal Ind.* **20**, 469-70(1922).—Polemical. The use of insol. anodes and salts of the metal in the deposition of Cd eventually results in economic failures. Zn is cheaper and equal to Cd as a rust preventive. W. H. BOYNTON

Advantages of cadmium plating over zinc plating. C. H. HUMPHRIES. *Metal Ind.* **20**, 470-1(1922).—Polemical. Cf. preceding abstract. More beautiful finishes are obtained with Cd, they are more readily buffed and nickeled than Zn plated articles, and Cd is more rapidly deposited. W. H. BOYNTON

Small oil engine battery-charging sets. III. W. WILSON. *Beama* **12**, 39-43 (1923); cf. *C. A.* **17**, 26.—A number of complete sets are described. C. G. F.

The electrical precipitation of dust particles. SAGEY. *Rev. métal.* **19**, 703-16 (1922).—A review. A. P.-C.

The Cottrell process for the precipitation of dust. JULIEN RAICK. *Rev. métal.* **19**, 605-13(Abs.)(1922).—A review. A. P.-C.

Electrochemistry of organic compounds. ALEXANDER LOWY. *Ind. Eng. Chem.* **15**, 15-6(1923).—Org. compds. may be decomposed electrolytically as nonelectrolytes by action of products of decompn. of electrolytes. The reactions include oxidation, reduction, halogenation, synthesis, etc. A. H. DICK

Production of nitrogen oxides and ozone by high-voltage discharges. K. B. McEACHRON AND R. H. GEORGE. *Bull. Purdue Univ.* **6**, 1-189(1922).—The corona discharge has been used in the production of O_3 , but its technical use for the fixation of atm. N has been prohibited by the low concns. of N oxides obtained. Spiel (*Thesis, Techn.*

High School, Vienna, 1909) obtained as much as 5.6% of NO in air confined in a Siemens tube, and the original purpose of the present work was to apply Spiel's conclusions to a tube using moving air and obtain satisfactory yields of N oxides. Expts. with the Siemens type of tube confirmed the results of Spiel. Under the influence of the discharge a decrease in the pressure of the enclosed air occurred. After a time this decrease reached a max. and reversed. The yield of NO was always greater near the reversal point than after the pressure had increased to the initial value. In case the air in the tube had been in contact for a considerable time with other air, even in minute quantities, which had been previously subjected to elec. discharge, the pressure decrease was modified or eliminated altogether, the pressure rising instead of falling. Such contamination affected the appearance of the discharge, decreased the yield and under certain conditions prevented the formation of any absorbable products. It was not possible in most cases to account for the total pressure decrease on the basis of the amt. of O₃ and NO found, and therefore, the formation of some heavy mol. is suspected. As a rule the pressure did not decrease more than 60 mm. A corona discharge could be produced in fresh air at a lower voltage than in air that previously had been subjected to elec. discharge. Rod-type tubes were constructed by filling the annular space between 2 concentric glass tubes with glass rods. This kind of tube gives a uniform discharge without the formation of sparks. In one of these tubes (inside diam. of the annular space 2.4 cm., outside diam. 4.5 cm., and length 71 cm.) increasing the air velocity reduced the concn. of both N oxides and ozone but increased up to certain limits the yield per kw.-hr. The yields were better at 31 cycles than at 61 cycles. At 31 cycles 56.7 g. of O₃ per kw.-hr. with a concn. of 5.6 g. per cu. m. were obtained. A porcelain tube of 10.1 cm. outside and 7.6 cm. inside diam. was surrounded by a 15.2-cm. Al tube and contained a 5-cm. Al tube concentrically located. The spaces between the two Al tubes and the porcelain tube were filled with glass rods 0.63 cm. in diam. With this app. the highest yields of *nitric acid* were obtained at a current of 10 milliamps. The yield increased to a practically const. value at flow rates above 5 l. per min. With decrease in pressure (from 845 to 400 mms.) the yield of O₃ decreased and that of NO increased. With an air flow of 19.9 l. per min., a pressure of 845 mm., and a current of 10 milliamps., the yield of ozone was 66 g. per kw.-hr. with a concn. of 6.5 g. per cu. m. and the yield of HNO₃ was 2.9 g. per kw.-hr. with a NO concn. of 0.0139%. A 5-hr. run showed that some form of cooling would probably be necessary to prevent a decrease in yield owing to increased temp. A large single dielec. tube consisted of an Al rod (1.59 cm. in diam.) surrounded by a porcelain tube (7.6 inside diam. and 10.1 cm. outside diam.) which in turn was surrounded by an Al tube 14.1 cm. in diam., all parts being concentrically located. The active length of this tube was approx. 152 cm. The air passed down through the space between the Al and porcelain tubes and up through the inside of the porcelain tube. This app. gave a mixed discharge consisting of corona with a large number of static sparks, which decreased in number and length with decreasing pressure, until at 560 mms. they appeared for only a very short distance out from the Al rod. With an increase in air velocity at pressures slightly above the atmosphere, the yields increased rapidly, a peak being formed at an air flow rate of about 6 l. per min. In this app. the yield of N oxides decreases and that of O₃ increases with increasing pressure. At the point of max. yield of nitric acid, cyclic variations in the meter readings and manometer variations some times as great as 1 to 2 cm. of Hg take place. During the run a white fog containing nitric acid appears over the absorbing liquid. Tests on a tube in which the corona discharge was replaced by a spark discharge between two Al wires gave a concn. of NO as much as 3.87 vol. % at an air velocity of 0.0187 l. per min. Very small amts. of O₃ are produced by this type of discharge. An apparatus of the rod type, if properly cooled, gives yields of O₃ of sufficient magnitude, so that the tube

becomes of importance as a commercial ozonizer. The yields of NO per kw.-hr. were in all cases small compared to those obtained by the use of the commercial arc process.

D. MACRAE

New type of high-power vacuum tube. W. WILSON. *Bell. Techn. J.* 1, 4-17 (1922).—The development of methods of making vacuum-tight glass-to metal seals has made possible the construction of three-electrode vacuum tubes capable of delivering at least 100 kw. to an antenna. W. G. Houskeeper has found that heavy Cu leads may be sealed through glass provided that they be made into a ribbon with two sharp edges and that copper and glass tubing may be sealed together if the end of the copper tube be ground to a sharp edge. This second type of seal is used to provide the tube with a water-cooled anode consisting of a large copper thimble forming part of the vacuum tube envelope.

D. MACRAE

Neon glow discharge lamp on alternating current circuits. R. A. BRUCKBANK AND L. E. RYALL. *Electrician* 90, 4-6(1923).—Oscillograms are reproduced and discussed.

D. MACRAE

Power losses in insulating materials. E. T. HOCH. *Bell. Tech. J.* 1, 110-7(1922).—In ordinary insulation, where the object is to provide a mechanical separator or support, the product of phase difference and dielec. const. is a true measure of the energy loss per unit vol. At a frequency of 500,000 cycles the following values of *dielec. constant* and of the product of dielec. const. and *phase difference* in degrees were obtained by the resistance variation method: phenol-fiber A, 5.8, 16.8; wood (oak) 3.3, 6.7; wood (maple) 4.4, 8.4; wood (birch) 5.2, 19.2; hard rubber 3.0, 1.5; flint glass 7.0, 1.68; plate glass 6.8, 2.7; cobalt glass 7.3, 2.9; Pyrex glass 4.7, 1.18. For hard rubber at 21°, 71°, and 120° the dielec. const. was 3, 3.1, and 3.2 while the corresponding products were 1.5, 3.7, and 11.8. Similarly for Pyrex glass at 20°, 74°, and 125° the dielec. const. was 4.9, 5.0 and 5.0 and the products were 1.18, 2.0, and 3.5. ["Phenol-fibre" is not defined by H.]

D. MACRAE

Insulating oils are decomposed by passage of current; how to keep and restore their strength. E. J. GRALEY. *Coal Age* 22, 953-5(1922).—In general "transformer oil" includes oils in transformers, oil switches, lightning arresters and feed regulators. Changes in mol. structure cause changes in sp. gr., sp. heat, viscosity, volatility, dielec. strength and other properties. Phys. essentials for a good insulating oil are: high dielec. strength, high flash and burning points, low f. p., low viscosity, a min. tendency to form sludge, and freedom from acid, alkali, S, wax, oils and fats, and other sol. matter. Periodic inspection and testing are necessary. Specifications are given for oils to be subjected to various conditions.

W. H. BOYNTON

The electric steam generator. HORACE DREVER. *J. Ind. Eng. Chem.* 14, 923-5 (1922).—The elec. generation of steam by passing a. c. (usually high tension) directly through the water is economical for utilization of off-peak power and is generally profitable in localities where hydroelectric power is abundant but fuel is expensive. An elec. steam generator of 1000 kw. capacity is equivalent to a boiler of 100 h. p. (Cf. also *Elec. World* 80, 1211-2(1922)).

LOUIS JORDAN

Ceramic firing in electric furnaces (SMALLEY) 19. Melting and refining metals (Can. pat. 224,263) 9.

BROWN, H. G.: The Lead Storage Battery. London: The Locomotive Publishing Co. 5s. Reviewed in *Engineering* 114, 340(1922).

Storage battery. S. M. MEYER and W. JAMES. U. S. 1,437,986, Dec. 5. Structural features.

Storage battery. F. J. ERICKSON. U. S. 1,439,155, Dec. 19. Structural features.

Storage battery counter cell. W. E. KERSHAW. U. S. 1,437,470, Dec. 5. A H_2SO_4 electrolyte is used with a Pb anode and $\text{K}_2\text{Cr}_2\text{O}_7$ as a depolarizing agent.

Storage battery plate. B. FORD. U. S. 1,437,468, Dec. 5. Structural features.

Storage batteries plates. WM. H. WOOD. Can. 226,227, Nov. 21, 1922. Animal hair, from which the external scales have been removed, is mixed with oxide of Pb for battery plates. Cf. C. A. 16, 1188; 17, 242.

Galvanic cells. R. SCHUSTER. Can. 226,685, Nov. 28, 1922.

Galvanic primary cells. R. SCHUSTER. Can. 226,684, Nov. 28, 1922.

Reversible electric battery. V. C. GOODRIDGE. U. S. 1,436,873, Nov. 28. Grid-less batteries are formed with a positive electrode of Pb peroxide and a negative electrode of porous Pb. The electrode material may be retained within cellulose receptacles treated with Na silicate to prevent attack from SO_4 of a H_2SO_4 or ZnSO_4 electrolyte and plaster of Paris may be used for increasing the porosity of the electrode material. The battery is believed to operate by dissociation and recombination of the components of the H_2O present and is free from sulfating troubles.

Electric batteries containing zinc chloride. D. C. REED. U. S. 1,437,553, Dec. 5. See Can. 222,095 (C. A. 16, 3266).

Electric battery terminal. H. R. MITCHELL. U. S. 1,438,454, Dec. 12. Structural features.

Dry cell battery. A. A. MACKENZIE and R. C. BENNER. U. S. 1,437,603, Dec. 5. A protective layer is formed upon the inner surface of a Zn container electrode by applying ZnCl_2 or CaCl_2 and a starch or flour paste.

Dry cell battery. C. HAMBUECHEN. U. S. 1,438,110, Dec. 5. In prep. cells of the non-lining type, a gelatinizable material, such as cereal paste containing electrolyte salts, is placed in the lower portion of a Zn can and after gelatinizing the superficial portion a mix bobbin is inserted partially to displace the ungelatinized material.

Dry batteries of the "deferred action type." R. C. BENNER and H. F. FRENCH. U. S. 1,438,084-5, Dec. 5. Structural features.

Electrolytic cell. WM. G. ALLAN. Can. 226,653, Nov. 28, 1922. Each of a number of cell casing numbers has an assembling flange at one end cooperating in pairs. Each pair is held together by a removable clamp.

Electric cells. E. A. G. STREET. Can. 227,140, Dec. 12, 1922. A conductive porous coating of charcoal is pressed on to the positive electrode of ordinary C which projects above the electrolyte into the atm. thus allowing the circulation of gases used as depolarizers. The negative electrode is made of Zn and may form the container.

Electrolytic cells. A. E. KNOWLES. Can. 226,089, Dec. 12, 1922. An electrolytic plant for the production of O and H from water consists of a group of superimposed cells, with partitions between adjacent cells, electrodes extending upward from each partition to the cell above and electrodes extending downward from each partition into the cell below. The current leads connect to the upper closure of the topmost cell and the bottom of the lower cell of the group.

High-voltage copper-oxide depolarizer for electric batteries. R. C. BENNER and H. F. FRENCH. U. S. 1,438,086, Dec. 5. A depolarizing material which can give a potential at least 0.05 v. higher than roasted Cu scale under the same conditions is prepared by heating Cu-NH_4 compounds to effect decomposition or by decomposition of other Cu compounds at 240-500°.

Electrolytic anode. R. A. PRICE. U. S. 1,438,722, Dec. 12. Structural features of hooks and supporting bars of anodes such as are adapted for use with Zn anodes.

Projector electrode. W. R. MOTT. U. S. 1,439,016, Dec. 19. See Can. 224,495 (C. A. 16, 4148).

Electrode for copper deposition. C. G. FINK. U. S. 1,437,507, Dec. 5. Elec-

trodes resistant to anodic disintegration are formed of an alloy contg. Co and Si 11.5–13% with some Mn, Cr and C. Such electrodes are suitable for use in CuSO_4 solns. contg. chlorides or nitrates. See *Mining Mag.* 25, 256(1921).

Electrodes and electrolysis. H. PLAUSON. Can. 226,423. A conductive electrode of adjustable porosity, which is sufficiently porous and strong to allow liquid to be passed therethrough at high pressure during electrolysis, is made of small elements of conductive material held together about a central pipe having openings therein.

Electrolysis of water. R. PECHKRAZ. Can. 226,192, Nov. 21, 1922. A water decomposing app. of the filter press type has the metal electrodes sepd. by metal partitions as thin as paper and having very fine holes in the greater part of their surface.

Gas reactions in electrolytic cells. C. B. JACOBS. Can. 225,942, Nov. 14, 1922. An electrolytic cell for conducting gas reactions has porous electrodes made of graphitized petroleum coke, means for conducting gas into and through the pores of the electrodes, an electrolyte and means for conducting away the products of reaction. In *oxidizing N*, e. g., dil. HNO_3 is electrolyzed in a cell having a porous anode and N is passed through the anode during electrolysis to combine with the O liberated. NH_3 may be produced by electrolyzing NaOH in a cell having a porous cathode and passing N through the cathode to combine with the H liberated.

Electrolyte for use in the electrodeposition of metals. Q. MARINO. Can. 225,879, Nov. 14, 1922. An electrolyte for plating contains an alkali cyanide soln. of the reaction product of a Ni salt, NH_3 , an alkali borotartarate and an alkali formate, there being no substantial excess of cyanide. Cf. *C. A.* 16, 1365.

Electrolytic treatment of metalliferous materials containing metals of the chromium group. R. E. PEARSON and E. N. CRAIG. Can. 225,966, Nov. 14, 1922. Materials contg. a metal of the Cr group are placed in the anode compartment of an electrolytic cell with an electrolyte in which the material is insol. and a current is passed from the anode into the electrolyte. Crude U powder may then be purified at the cathode.

Basic magnesium hypochlorite. E. MERCK CHEM. FAB. Ger. 305,419. Addn. to 297,874. Apr. 30, 1918. The addition of magnesia required in the original patent in the electrolysis of MgCl_2 need not be made at the beginning of the process, but rather, when the electrolysis is completed, MgO or $\text{Mg}(\text{OH})_2$ is introduced into the electrolyte.

Nitric acid by the electric arc. W. SIEBERT. Can. 226,263, Nov. 21, 1922. In obtaining HNO_3 by means of the elec. arc in a closed cycle a temp. below -10° is maintained in the last portions of the absorption installation so that the content of steam in the O and N gases led back to the furnace is reduced to a practically irrelevant amt.

Apparatus for oxidation of atmospheric nitrogen. B. THOMAS. U. S. 1,437,569, Dec. 5. A hollow center electrode is mounted along the axis of an outer annular electrode and gases passing between the electrodes are given a whirling movement around the axis.

Electric furnaces. W. E. MOORE. Can. 226,309, Nov. 21, 1922. In the manuf. of steel or other metals in an elec. furnace current is supplied to the bath from a plurality of arcing electrodes and the amt. of current passing through the bath is varied by varying the length of one or more of the arcs with respect to the others. The melt may be produced by means of a high voltage and long arc and refined with substantially the same current with reduced voltage and shorter arc.

Electric furnaces. W. E. MOORE. Can. 226,310, Nov. 21, 1922. In the treatment of steel or other metals in an elec. furnace supplied with power from a multiphase circuit, a circulation of the bath is produced by a rectified current from the current of sep. phases. Two or more currents of different phases may pass from the electrodes to the bath and the amt. of current passing through the bath may be varied by unbalancing the resistance of the arcing circuits.

Electric metallurgical furnaces. W. E. MOORE. Can. 226,311, Nov. 21, 1922. The furnace has a chamber adapted to contain metal, an elec. arc in the upper part of the chamber for heating the metal, a pair of extensions on the furnace bottom angularly disposed with respect to each other and to the central axis of the furnace. Each extension has a channel in the form of a loop of elongated transverse section which gradually expands upwardly into communication with the main chamber and an elec. heating element around which each extension is looped.

Electric furnace. F. T. SNYDER. Can. 226,318, Nov. 21, 1922. A furnace having refractory heat insulating walls and an arc resistor with a negative temp. coeff. is started with a long arc at high voltage and small current and the heat is furnished with a short arc at low voltage and high current.

Electric furnaces. L. RENNERFELT. Can. 226,027, Nov. 14, 1922. The furnace has a plurality of electrodes suspended into a projection from the bottom of the furnace under the electrodes, a conducting layer of C on the projection forming contacts for the ores formed, and a channel along the heating zone of the arcs for receiving the material to be heated.

Electric reverberatory furnace adapted for smelting ores. R. M. KEENEY. U. S. 1,438,381, Dec. 12.

Induction furnaces. J. R. WYATT. Can. 226,811, Dec. 5, 1922. The furnace has a pool for molten metal, walls forming a closed channel below the pool, the channel communicating with the pool at two points and having parts of the channel forming an acute angle at a distance from the pool and a transformer for which the metal in the channel acts as secondary, setting up motor effect in the channel.

Electrode holders for electric furnaces. J. H. GRAY. Can. 226,049, Nov. 14, 1922. An electrode holder has a water-cooled supporting arm which conducts the current to the electrode and flexible cables which extend to a fixed point above the arm.

Electrode holder for electric furnace. JNO. YOUNG. Can. 226,035, Nov. 14, 1922. An electrode holder comprises an electrode supporting arm, a block secured thereto and insulated therefrom, water-cooled means carried by the block for clamping the electrode in position and water-cooled current-conductors connected with the clamping means.

Electrode holders. B. D. SAKLATWALLA and A. N. ANDERSON. Can. 226,046, Nov. 14, 1922. An electrode holder has an opening with a tapered ring removably seated in the opening and wedges adapted to be driven between the tapered ring and the electrode. The outer casing and current condition are water-cooled.

Electrode holder. E. W. HUGHES. Can. 226,016, Nov. 14, 1922. An electrode holder has passages for the circulation with water-cooled current-conductors. The supporting arm carries a contact and arms which carry separate contacts and stops for limiting the opening movement of the arms.

Fusing silica in an electric furnace. A. EIMER. U. S. 1,438,936, Dec. 12. SiO_2 is first heated by an elec. resistor to bring it to a condition of semi-fluidity and is then more highly heated by an elec. arc completely to fuse it.

Terminal protector for electrolytic condensers and rectifiers. J. COULSON and C. J. ROTHMANN. U. S. 1,438,636, Dec. 12. Terminals which may be formed of Al are surrounded by a sleeve above the level of the electrolyte, to maintain a H_2O -satd. atm. around the terminal, which prevents corrosion of the terminals.

Heat-treating electrical resistance units. L. T. RICHARDSON. U. S. 1,439,123, Dec. 19. Resistance units are heat-treated to coat them with fused glass, while embedded in inert material such as sand.

Electric incandescent lamps. JUST-FÉLE IZZÓLÁMPA ÉS VILLIAMOSSAGI GYÁR RÉSVENYTÁRSASÁG. Brit. 185,732, Aug. 29, 1922. A lamp of the inert-gas-filled type

is given a content of P or P compd. exceeding 0.1% of the wt. of the incandescent body and contains gas at a pressure of less than 0.1 of an atm. The P may be introduced as a coating on the filament or by making the filament of a W alloy high in P. It may also be replaced wholly or in part by other elements of the P group, such as S, Sb, As, Se, or Te, or by compds. of these, such as Sb or As sulfide. In one method of making the lamp, the frame is covered with P before the bulb is put on. The lamp is heated on the pump in an air bath at 400° and the filament raised to incandescence. The P is allowed to vaporize for some time and after the current has been cut off and the pump cooled, less than 0.1 atm. of inert gas is introduced. During the evacuation, the lamp may be cleansed by introducing and drawing off H₂. Lamps so heated give a reduced blackening and when filled with pure A are less liable to arc and discharge through the gas.

5—PHOTOGRAPHY

LOUIS DERR

Energy exchanges in the formation of the latent image of a photographic emulsion. S. E. SHEPPARD AND E. P. WIGHTMAN. *J. Opt. Soc. America* **6**, 913 (1922).—When light falls upon a AgBr grain the possible energy changes are (1) energy of sepn. of Ag⁺ from Br⁻ in the lattice structure, (2) energy of the loss of an electron by the Br⁻ ion, (3) energy of the addition of an electron to the Ag⁺ ion, (4) energy of formation of the Br₂ mol., (5) energy of formation of Br addition product with gelatin, (6) energy of formation of Br substitution product with gelatin, (7) energy of loss of an electron by the Ag mol. or atom. Of these the first 5 appear to be the most probable, but the seventh may play an important catalytic part.

L. DERR

Silver iodide and methylene blue B. K. C. D. HICKMAN. *Phot. J.* **62**, 512-21 (1922).—Among the many inorg. ppts. which attract dyes from soln. to form colored lakes AgI is notable. In the dye-toning processes the Ag of the image is converted into AgI, washed, immersed in the dye-bath, and again washed thoroughly to discharge the color from the region not occupied by the image. For methylene blue B pure AgI has very little affinity; this is, however, increased by contamination with other iodides. Two sep. types of dyed ppts. were investigated and the results compared with AgI in the photographic plate. A scheme of analysis is outlined for the detn. of small quantities of the dye in AgI.

L. DERR

Desensitizing in its commercial aspect. A. C. BANFIELD. *Phot. J.* **62**, 542-5 (1922).—With pinakryptol green as desensitizer, there is an advantage in the greatly increased light in the dark room and a great saving of time through the possibility of handling a much larger number of plates at one time. In the brighter light densities are more easily judged, yet there is no staining and no fog.

L. DERR

Photographic sensitizing dyes. S. PALKIN. U. S. 1,437,674, Dec. 5. Photographic sensitizing dyes of the dicyanin type are prepd. by the interaction of Na sulfide and CHCl₃ in alc. soln. with quaternary halide addition products of the α, γ dimethylated quinoline derivs., e. g., 2,4-dimethyl-6-ethoxyquinoline ethiodide.

Ethyl cellulose solution. S. J. CARROLL. U. S. 1,437,792, Dec. 5. A compn. adapted for making *photographic films* is formed of ethylcellulose dissolved in a mixt. of about equal amts. of monochloronaphthalene and EtOH. Cf. *C. A.* **17**, 467.

Cellulose ether composition for coating films. A. F. SULZER. U. S. 1,437,828, Dec. 5. A composite soln. adapted for backing nitrocellulose photographic films is prepd. by mixing separately prepd. solns. of nitrocellulose or acetyl cellulose dissolved in acetone and cellulose ethyl ether dissolved in EtOH and CHCl₃. U. S. 1,437,829 specifies an antistatic film formed mainly of nitrocellulose with a coating layer formed

of cellulose acetate and ethylcellulose dissolved in a mixt. of CHCl_3 , alc. and acetone.

Color screen for color photography. K. E. STUART. U. S. 1,439,035, Dec. 19. A color screen is prepd. with colored bands having overlapping spectra.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

The formation of carbon disulfide by the interaction of sulfur dioxide and charcoal. B. RASSOW AND K. HOFFMANN. *J. prakt. Chem.* 104, 207-40(1922).— SO_2 was passed through glowing wood charcoal with the formation of CS_2 ; by a new and exact analytical method the course of the reaction was followed at different temps. At 700° only traces of CS_2 are formed. Above 750° CS_2 increases; COS , CO_2 , S and a very small amt. of CO are present. At 850 – 900° the formation of CS_2 reaches a max. when the S from the SO_2 is divided as follows: 35% to CS_2 , 55% to COS and 10% free S, with CO and only a small amt. of CO_2 making up the balance of the exit gases. Above 900° the CS_2 and COS decrease, with the O of the SO_2 forming almost entirely CO. Above 1100° S and CO are the products of reaction; no more CS_2 could be detected and only traces of COS . Under the best conditions of slow gas flow, carefully purified wood charcoal, complete exclusion of H_2O and free O_2 , only a small amt. of SO_2 is converted into CS_2 and over 50% into COS which makes the process unfit for tech. purposes as no use can be made of COS which is easily exploded when mixed with air, decomposes rapidly with H_2O and has a very low condensation point. For analysis the exit gases were cooled to deposit S, passed through a soln. of Et_3P (Hofmann, *Ber.* 4, 207(1871)) in 5 parts abs. Et_2O which deposits the red addn. product (A) of CS_2 (cf. C. A. 1, 1982), then passed into a soln. of concd. NH_4OH and CaCl_2 which forms NiH , thiocarbamate (B) with the COS and CaCO_3 with the CO_2 ; this soln. when treated with neutral H_2O_2 and heated to boiling converts B into $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{CO}_3$ from which CaCO_3 ppts.; the ppt. after washing with CO_2 -free H_2O is dissolved in 0.5 N HCl, phenolphthalein added and titrated with 0.5 N NaOH; this gives the total CO_2 , part of which was from the oxidation of COS . The filtrate contg. CaSO_4 and $(\text{NH}_4)_2\text{SO}_4$ is evapd. to remove excess NH_3 , acidified with HCl, pptd. with BaCl_2 and the COS calcd.; the remainder of the exit gases consists of CO and traces of N_2 ; the CO was detd. with $\text{NH}_3\text{-Cu}_2\text{Cl}_2$. A is collected on a Gooch crucible, washed with H_2O , dried in a desiccator and weighed as Et_3PCS_2 . Many references are given to the literature on the formation and thermochemistry of CS_2 . N. A. LANGR

Action of nitric oxide and hydroxylamine compounds upon tertiary sodium arsenite. A. GUTMANN. *Ber.* 55B, 3007-12(1922); cf. C. A. 6, 1619; 9, 1053.—NO and Na_3AsO_3 react with evolution of heat to give N_2O and Na_2AsO_4 . The same reaction occurs if the NO is dissolved in K_2SO_4 ($\text{K}_2\text{SO}_3\text{-N}_2\text{O}_2$). PhNO and Na_3AsO_3 react when heated on the H_2O bath to give $(\text{PhN})_2\text{O}$ and Na_3AsO_4 . Two mols. NO react with PhNO with the liberation of 1 O and the formation of N_2O and $(\text{PhN})_2\text{O}$. The products of the interaction of $\text{Na}_2\text{Fe}(\text{CN})_2\text{NO}$ and Na_3AsO_3 are the same as if NaOH were present ($\text{Na}_4\text{-Fe}(\text{CN})_6$, NaNO_2 , NaCN and $\text{Fe}(\text{CN})_2$) *i. e.*, the NO in this case has no oxidizing properties. NH_2OH oxidizes Na_3AsO_3 to Na_2AsO_4 , NH_3 being the other product. There is some decompn. of NH_2OH into NH_3 , N_2 and H_2O . PhNHOH likewise oxidized Na_3AsO_3 and gives PhNH_2 and $(\text{PhN})_2\text{O}$. The isomeric *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$ has no action. Et-NHOH oxidizes the arsenite, and gave EtNH_2 . PhMe_2NO is reduced to PhNM_2 . Quinine oxide is reduced to quinine, with the formation of Na_2AsO_4 . These examples show that Na_3AsO_3 is a special reagent for tetravalent reactive O. C. J. WEST

Silicon hydrides. XI. Action of oxygen on SiH_4 and Si_2H_6 . ALFRED STOCK AND CARL SOMMERST. *Ber.* 55B, 3961-9(1922); cf. C. A. 15, 3951.—The explosive reactivity of these compds. toward O has been previously noted. The reactions of SiH_4

and Si_2H_6 with O, air and O-N mixts. still lower in O was quant. studied at temps. from -70° to -140° and under greatly reduced pressure. Even under these conditions the reaction is vigorous, often violent. Considerable amts. of H_2 were always formed which could not result from hydrolysis of primary oxidation products at the temps. of expt. as these are not very reactive toward water even at room temp. Apparently this H_2 is a primary product resulting from reactions such as $\text{SiH}_4 + \text{O} = \text{SiH}_3(\text{O}) + \text{H}_2$. The detonations characteristic of these reactions result from ignition of the resulting detonating gas when the temp. of the reaction has become sufficiently high. Considerable water was always formed and probably results from hydroxyl derivs. formed at low temp. but unstable at room temp., e. g., $\text{SiH}_2(\text{OH})_2 = \text{SiH}_2(\text{O}) + \text{H}_2\text{O}$. The solid residue of polymers of $\text{SiH}_2(\text{O})$ usually contained free Si resulting from strong local heating with deficiency of O.

A. R. MIDDLETON

Magnetic analysis of silicates and the silicic acids. PAUL PASCAL. *Compt. rend.* 175, 814-6(1922).—By studying the magnetic susceptibilities of the various hydrates of silica P. found that they behave magnetically like mixts. of anhyd. silica and water. This is an argument against the existence of definite silicic acids. J. A. ALMQUIST

Preparation of green manganese sulfide. F. L. HAHN. *Z. anorg. allgem. Chem.* 121, 209-10(1922).—The analytical procedure of Seeligmann (*C. A.* 9, 40, 1884), which invariably gives the green sulfide, is modified for prepn. of larger amts. Dissolve 100 g. MnSO_4 crystals in 300 cc. water. To prep. colorless NH_4 sulfide sat. 100 cc. of 20% NH_4OH with H_2S and add 100 cc. H_2O . To prep. yellow NH_4 sulfide sat. 30 cc. of the colorless NH_4 sulfide soln. with S at the b. p., cool, and dil. to 100 cc. with the colorless soln. In a large beaker heat to boiling 100 cc. water, 20 cc. 20% NH_4OH and 5 cc. of the MnSO_4 soln. and add, all at once, 30 cc. of the yellow NH_4 sulfide soln. The pptd. MnS becomes dark green at once. Add the colorless and the yellow NH_4 sulfide solns. at once and add the MnSO_4 soln., previously warmed, in small portions with const. stirring, keeping the mixt. nearly boiling. If too much MnSO_4 soln. is added at one time, pink sulfide forms but changes into the green form on stirring. The sulfide settles well and can be washed readily and dried in a current of H_2S or, if washed finally with EtOH , can be dried in a vacuum desiccator.

A. R. MIDDLETON

Germanium hydride. RUDOLF SCHENCK with ALBERT IMKER. *Rec. trav. chim.* 41, 569-75(1922).—(In German.) After trying various methods for breaking down arygrodit (the Ge mineral used) the original method of Winkler (*J. prakt. Chem.* 36, 207 (1887)) was preferred. It is described. Penfield's (*Z. Krist.* [3] 23, 243(1894)) method was also used. The quant. detn. of Ge in arygrodit by heating in dry Cl will be described elsewhere. Since GeO_2 reacts too violently with Mg it was first reduced with H_2 and mixed with 2 parts Mg powder and heated in Fe boats in a hard glass tube to give a crumbly gray-black mass. This material gave GeH_4 by Stock's method (*C. A.* 8, 1248; 12, 547) for BH_3 . Even after cooling the gases with liquid air the H_2 still contained GeH_4 . By passing these gases through wash bottles contg. AgNO_3 soln. the unpleasant physiol. effects of GeH_4 were avoided. The Mg-Ge alloy when treated with 5 N HCl gives GeHCl_3 as a volatile by-product. GeHCl_3 in contact with O_2 gives GeCl_2O ; with H_2O it gives a yellow ppt. of basic chlorides which with NaOH gives either $\text{Ge}(\text{OH})_2$ or HGeO_2H (Hantzsch). These side reactions cause losses which were prevented by using H_2SO_4 instead of HCl. The crude GeH_4 which might have been composed of several hydrides was purified by sublimation in Stock's app. (*l. c.*); pure GeH_4 m. -165° and b₇₆₀ -126° . The vapor tension of GeH_4 is given for 20 temps. lying between -164° and -125° . At the temp. of liquid air GeH_4 has a small vapor tension (less than 3 mm.) which was not detd. In 3 trials the mol. wt. as detd. by Regnault's method of weighing the vapor, all precautions being used, was found to be 78.06, 78.34, 76.38 (calcd. 76.50 for GeH_4). The hydride was thus found to be pure GeH_4 . This was

also confirmed by detg. the H_2 after decomposing the hydride by a method which is described in detail. The decompn. of GeH_4 takes place easily. It is only necessary to heat a point in a glass tube gently to decompose GeH_4 passing through it. The Ge mirror resembles that of As but is nonvolatile. Fresh NaOCl dissolves both mirrors but concd. HNO_3 oxidizes Ge to white GeO_2 while As gives sol. H_2AsO_4 . Concd. $AgNO_3$ gives a gray coloration with GeH_4 while with AsH_3 it gives a yellow compd. that becomes black on treating with H_2O . Over Hg GeH_4 decomposes somewhat in several days.

E. J. WITZEMANN

Crystallized sodium silicate. A. H. ERDENBRECHER. *Z. anorg. allgem. Chem.* **124**, 339-54(1922); cf. *C. A.* **16**, 879.—Analysis does not solve the problem of the hydrates of Na_2SiO_3 satisfactorily. A cryst. mass whose analysis corresponded to $Na_2SiO_3 \cdot 10H_2O$ had no definite m. p. When heated to 41° for 10 hrs., it sepd. into solid $Na_2SiO_3 \cdot 9H_2O$ and a liquid. Curves of the m. ps. of various mixts. of $NaSiO_3$ and H_2O indicated that there were no hydrates between $Na_2SiO_3 \cdot 6H_2O$ (m. 62.3°) and $Na_2SiO_3 \cdot 9H_2O$ (m. 47°). In order to stir the stiff pulps they were dild. with paraffin oil which was found to have no effect on the m. ps. Both m. p. and vapor pressure curves indicated $Na_2SiO_3 \cdot 14H_2O$, m. 37.2° , but no crystals were obtained. Unexplained changes were indicated at 41° and 30.5° . It was not satisfactory to det. the m. ps. by cooling because of pronounced undercooling and low velocity of crystn.

WM. STERICKER

Sodium chromite. ERICH MÜLLER. *Z. angew. Chem.* **35**, 557-8(1922).— $Cr(OH)_3$ was pptd. by NH_3 and dried over H_2SO_4 . Approx. a hexahydrate resulted. The soly. of this material was detd. in solns. of 5-18 *N* NaOH. For a given concn. of alkali at 18° soly. depended on duration of shaking, increasing to a max., then decreasing to a nearly const. value. Shaking for 40 hrs. at 70° , then 40 hrs. at 18° gave const. values but considerably lower than those obtained by shaking at 18° only for 10-14 days. The change of soly. appears to depend on aging of the hydroxide. The same increase to a max. followed by decrease was observed with increasing concn. of NaOH. The soly. curves of Cr_2O_3 show the same form but the soly. is much lower.

A. R. M.

The irido-dipyridino-tetrachlorides. MARCEL DELÉPINE. *Compt. rend.* **175**, 1075-7(1922).—D. gives complete directions for prepg. the two irido-dipyridino-tetrachloride isomers $[Ir(C_5H_5N)_2Cl_4]M$. Using Werner's theory of octahedrons D. assigns the *trans*-form to the red and the *cis*-form to the orange isomer. The K, Rb, Cs, NH_4 , Na, Tl and Ag salts have been prepd. The chem. properties of each isomer are given.

R. CHESTER ROBERTS

Anodic formation of pure lead tetracetate, lead tetrapropionate and silver diacetate. C. SHALL AND W. MELZER. *Z. Elektrochem.* **28**, 474-7(1922).—An anolyte consisting of 85 g. Pb acetate + 35 g. anhyd. Na acetate in 230 cc. of 99.4% HOAc (+ 2 g. H_2O), and a catholyte of 20 g. Na acetate + 12 g. Pb acetate were electrolyzed in a diaphragm cell between a rotating Pt anode (9.4 $cm.^2$) and a Pb cathode (70 $cm.^2$), with a current-strength of 0.28 amp. at a p. d. of 70 v. The temp. was 35° . At the end of 4 hrs., 3.5 g. pure Pb tetracetate had sepd. at the anode, while 2.67 g. remained in the electrolyte; this corresponded to a current yield of 80.02%. Pb tetrapropionate and Ag diacetate have been prepd. in a similar way. The yield of the former was very small and that of the latter was still smaller.

H. JERMAIN CREIGHTON

The preparation and properties of organic chlorostannites and -stannates. V. The salts of certain special bases. J. G. F. DRUCK. *Chem. News* **125**, 265-7(1922); cf. *C. A.* **16**, 2457.—*N*-Hydroxylamine chlorostannate was prepd. from $NH_2OH \cdot HCl$ + $SnCl_4 \cdot 5H_2O$ in dil. HCl. White crystals, sol. in cold H_2O ; hydrolyzed on heating; insol. in org. solvents except EtOH; does not m. 300° . *5*-Aminoquinoline chlorostannite: from 5-nitroquinoline; tin and concd. HCl. Pale yellow prisms, m. 160° . *5*-Aminoquinoline chlorostannate: 5-aminoquinoline, $SnCl_4$ and 8 : 5 HCl. Orange crystals on cooling, sol. in

water, cloudy on warming; soln. strongly acid; no ppt. with HgCl_2 but with H_2S forms SnS_2 . Insol. in org. solvents except hot MeOH and EtOH . M. 242° . *6-Aminoquinoline chlorostannite*: from 6-aminoquinoline, tin and 1 : 1 HCl . Feathery deliquescent crystals, sol. in cold H_2O . White ppt. with HgCl_2 , turning grey. Dark brown ppt. with H_2S water. Sol. in hot glacial AcOH ; slightly sol. in boiling EtOH ; deep red color with hot AmOH . Insol. in other common org. solvents. Decomposes at about 180° . *6-Aminoquinoline chlorostannate*: from 6-aminoquinoline, SnCl_2 and 1 : 2 HCl . Colorless nacreous plates, sol. in cold H_2O , gradually hydrolyzes. Sol. in hot alic. only. M. $224-8^\circ$. *Isoquinoline chlorostannate*: from isoquinoline, SnCl_2 and dil. HCl . Colorless crystals, darkening at 240° , m. 265° . Somewhat sol. in cold H_2O , hydrolyzed by hot H_2O . Sol. only in hot EtOH , MeOH , PhNO_2 and glacial AcOH .

M. O. LAMAR

Prussian blue and Turnbull's blue. V. ERICH MUELLER. *J. prakt. Chem.* **104**, 241-58(1922); cf. *C. A.* **3**, 1375; **4**, 727; **6**, 547; **8**, 3862.—The following substances are formed when $\text{K}_3\text{Fe}(\text{CN})_6$ is slowly added to FeCl_3 . They appear in the order stated except that the second appears as a temporary ppt. before the first one. $\text{Fe}'''\text{Fe}_4[\text{Fe}(\text{CN})_6]_b$, $\text{KFe}'''\text{Fe}(\text{CN})_6$, $\text{K}_3\text{Fe}'''\text{Fe}(\text{CN})_6$, $\text{K}_3\text{Fe}(\text{CN})_6$. When $\text{K}_3\text{Fe}(\text{CN})_6$ is added to FeCl_3 the following are formed: $\text{KFe}'''\text{Fe}_4[\text{Fe}(\text{CN})_6]_b$, $\text{KFe}'''\text{Fe}_3[\text{Fe}(\text{CN})_6]_b$, $\text{KFe}'''\text{Fe}(\text{CN})_6$ and $\text{Fe}_4[\text{Fe}(\text{CN})_6]_b$. The reactions are followed by means of electrometric titrations and the fact that all of the insol. substances are capable of forming solid solns. with each other is demonstrated.

M. O. LAMAR

Action of H_3BO_3 on mannitol (DUBRISAY) 2.

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Contradictions and errors in analytical chemistry. I. The precipitation of aluminium with thiosulfate and its separation from iron. F. L. HAHN AND G. LEIMBACH. *Ber.* **55B**, 3161-3(1922).—The attempt is often made to sep. Fe^{+++} and Al^{+++} by boiling the slightly acid soln. with $\text{S}_2\text{O}_3^{--}$ and finally adding a little NH_4OH . Expts. indicate that the pptn. of Al under these conditions is not quite complete and that a little Fe is likely to be carried down by the alumina ppt. If the boiling is not continued too long there is but little Al left in soln. and if PhNHNH_2 is used instead of NH_4OH there is less danger of contamination with Fe . **II. Old thiosulfate solutions in volumetric analysis.** F. L. HAHN AND H. WINDISCH. *Ibid* 3163 5.—It has been assumed that thiosulfate solns. gain in strength because of the slight acidity of the water, due to CO_2 perhaps, and that the acid liberates $\text{H}_2\text{S}_2\text{O}_3$ which breaks down into H_2SO_3 and S . W. is unable to detect any sulfite in an old soln. of $\text{Na}_2\text{S}_2\text{O}_3$ but does find that a little alkali hydroxide tends to prevent decompn. of the $\text{S}_2\text{O}_3^{--}$ and the gain of strength on standing.

W. T. H.

Quantitative analysis by means of the refractometer and interferometer. J. BRČKA. *Z. physiol. Chem.* **121**, 288-99(1922).—When a reaction occurs on mixing 2 solns. the n observed is different from the value calcd. from the refractions of the 2 solns. The difference is directly proportional to the concn. of the resulting compd. This principle has been applied to pptn. reactions and leads to the formula $\% = F(a+b)d/a$. In words, this states that the percent of the substance pptd. from a g. of soln. is directly proportional to the wt. of the mixed solns. ($a + b$) and to the difference (d) of the calcd. and found n s. and inversely proportional to the amt. (a) of pptd. soln. The values of F for the detn. of SO_4^{--} and Cl^- have been detd. and the concn. limits for which

the equations hold are given. The interferometer may be substituted for the refractometer.

R. L. STEHLÉ

Colloid problems in analytical chemistry. HENRY BASSETT. *Brit. Assoc. Advancement of Sci.* 4th Rept. 1922, 5-23; *Chem. Trade J.* 71, 413-5.—This paper considers mainly gravimetric analysis, and attempts to treat "colloidal" phenomena as being explicable in terms of chem. combination and ionization.

JEROME ALEXANDER

A modified methyl orange indicator. K. C. D. HICKMAN AND R. P. LINSTREAD. *J. Chem. Soc.* 121, 2502-6(1922).—The eye is most sensitive to a change in hue when one of the shades is of neutral tone. A series of expts. were tried with various dyestuffs added to methyl orange to see if it would be possible to develop an indicator such that the methyl orange end point would be easier to detect. By dissolving 1 g. of methyl orange and 1.4 g. of xylene cyanole FF in 500 cc. of 50% alc., an indicator soln. is obtained which has all the desirable qualities of methyl orange and a more characteristic end point. In titrating NaOH with 0.1 N HCl, and using 2 drops of the indicator, the soln. remains green to within 2 drops of the end point, then becomes grayish green and steel-gray at the end point which is at $p_H = 3.8$. Further addn. of acid produces a magenta shade. The titration corresponds to the salmon-pink shade with methyl orange rather than to the beginning of the change from yellow to red. The new indicator can be used to advantage for all titrations where methyl orange has been recommended but will not give satisfactory results in the titration of weak acids. At night time, the end point can be easily seen when illumination is obtained with a 100-watt, gas-filled, "daylight" lamp with a blue bulb.

W. T. H.

Titration curves of some common acids and bases as determined by the hydrogen electrode. C. E. DAVIS, E. T. OAKES AND H. M. SALISBURY. *Ind. Eng. Chem.* 15, 182-90(1923).—A set of electrometric titration curves is given, in which the same standard procedure was followed in each case, for HCl, H₂SO₄, H₃PO₄, primary Ca phosphate and citric acid when titrated with NaOH and with Na₂CO₃.

W. T. H.

The use of pernitric acid for analytical purposes. IW. TRIFONOW. *Z. anorg. allgem. Chem.* 124, 136-9(1922); cf. *C. A.* 17, 36.—(a) *Detection of nitrites.*—To the unknown soln. add a few drops of PhNH₂, shake thoroughly and acidify with 5-10 cc. 2.0 N H₂SO₄ according to the vol. of the soln. In the presence of nitrite the liquid is colored a fine yellow. Sensitiveness 1:1,000,000. (b) *Detection of H₂O₂.*—To the unknown soln. add 2-3 drops of a 3% NaNO₂ soln., shake thoroughly and acidify with 5-10 cc. 2.0 N H₂SO₄. In the presence of H₂O₂ a bright yellow color is produced. Sensitiveness 1:300,000. (c) *Direct detection of benzene* in the presence of toluene, xylene and aliphatic hydrocarbons: To about 5 cc. of the unknown liquid add 5-10 cc. of a mixt. of equal vols. of 3% H₂O₂ and 4% NaNO₂ (or 5% KNO₂), emulsify by shaking and add 2-3 cc. 2.0 N H₂SO₄. Shake thoroughly. After several min. pour off the hydrocarbon layer. Place not more than 5 cc. of the yellow aq. layer in a test-tube and add a small piece of solid alkali hydroxide. In the presence of benzene a red ring is formed around the piece of caustic; also the concd. alk. layer is colored a beautiful red; with large amts. of benzene the whole mass is an intense dark red. The sensitiveness is not great. (d) *Direct detection of benzene in alcohol:* Mix thoroughly several cc. of alc. with the above H₂O₂ and NaNO₂ test solns., acidify with 1-2 cc. 2.0 N H₂SO₄, shake and boil 1-2 mins. Cool to room temp., and to 2 cc. of the mixt. add a few drops of concd. KOH or NaOH. Benzene produces an orange-red color. In the absence of benzene there is a slight yellow turbidity due to the resinification of the aldehyde. The sensitiveness of the method is fairly good. The easy oxidation of alc. to aldehyde by pernitric acid may well be applied to analysis.

M. O. LAMAR

A rapid gas-volumetric method for determining carbonic acid in carbonates. C. TUBANDT AND H. WEISZ. *Chem.-Ztg.* 46, 1105(1922).—A patented app. is described

which permits the detn. of the CO_2 content in about 15 min. The sample is decompd. with a slight excess of HCl and the soln. is boiled vigorously to remove all of the CO_2 from the decompn. flask, the vapors being passed through a condenser. The vol. of CO_2 evolved is read directly.

W. T. H.

The reducing action of ferrous hydroxide. SUSUMU MIYAMOTO. *Japan J. Chem.* 1, 57-80(1922); *Sci. Papers Inst. Phys. Chem. Research* 1, 31-55(1922).—An English translation of a paper previously published in Japanese (*C. A.* 16, 3042).

K. K.

Test for the nitrous anion. P. FALCIOLA. *Gazz. chim. ital.* 52, II, 87-9(1922).—The HNO_2 test for $\text{H}_2\text{S}_2\text{O}_3$ may be reversed and used as a test for NO_2^- ; 0.5 N $\text{Na}_2\text{S}_2\text{O}_3$ may be added to an alk. nitrite (even 0.00001 N) acidified with H_2SO_4 with which it gives a yellow color. The test is as sensitive for NO_2^- as for $\text{S}_2\text{O}_3^{--}$ but not nearly so sensitive as the reagent of Griess for instance. One l. H_2O with 2 cc. H_2SO_4 , an excess of thiocyanate and then 0.1 g. FeSO_4 is a reagent that gives an orange coloration with a 0.0001% aq. soln. of NaNO_2 and slowly with a 0.00001% soln. The FeSO_4 must be pure and may be freshly prepd. by placing a bit of iron in dil. H_2SO_4 and with this the blank test remains colorless for hrs. (cf. Horst, *C. A.* 15, 3054). Aniline phosphate (as well as other salts of PhNH_2) with alkali nitrites gives a yellow color in dil. soln. or a red color with more concd. solns., which is resistant to heat. The limit of sensibility does not exceed 1:100,000. For the best results the solns. should be allowed to stand for some time out of contact with air. The colored substances pass into soln. when agitated with C_2H_6 . The test is not particularly valuable, since PhNH_2 salts give similar results with HCO_2H , AcOH , etc.

E. J. WITZERMANN

Notes on gravimetric analysis. XXI. L. W. WINKLER. *Z. angew. Chem.* 35, 662-3(1922).—26. **The determination of lead.** In the absence of much free HNO_3 , the detn. of Pb as PbSO_4 using $(\text{NH}_4)_2\text{SO}_4$ as precipitant gives accurate results without the addition of alc. To 100 cc. of neutral soln. contg. the equivalent of about 0.35 g. Pb as nitrate or chloride, add 1 cc. of N HNO_3 and heat to boiling. Remove the beaker from the source of heat and add, in a thin stream, 10 cc. of 10% $(\text{NH}_4)_2\text{SO}_4$ soln. while stirring. Do not add the reagent so that it runs down the sides of the beaker containing the Pb soln. After a few min. stir again and then allow the contents of the beaker to stand overnight. Filter with suction and wash with a cold, satd. PbSO_4 soln. Dry at 130° for 2 hrs. Cf. *C. A.* 16, 2460.

W. T. H.

Rapid determination of potash in acid-insoluble silicates. M. M. GREEN. *Ind. Eng. Chem.* 15, 163(1923).—The sample is decompd. with HF and HClO_4 and the residue extd. with hot water. By evapn. to fumes of HClO_4 an impure residue of KClO_4 is obtained which is insol. in alc. By filtering, dissolving the ppt. in water and reprecipg., pure KClO_4 is obtained and an accurate detn. of K_2O in a silicate finished in less than 3 hrs.

W. T. H.

Determination of chromium and iron in commercial solutions of chromium salts. E. MACQUERON. *Rev. prod. chim.* 25, 799-800(1922).—The Cr is oxidized in alk soln. with Na_2O_2 , the $\text{Fe}(\text{OH})_3$ is filtered off, and the Fe and Cr are detd. by KMnO_4 titrations.

A. P.-C.

A peculiar catalytic reaction which may serve for the detection and determination of copper and for a lecture experiment. F. L. HAHN AND G. LEIMBACH. *Ber.* 55B, 3070-4(1922).—When Fe^{+++} ions are in contact with $\text{S}_2\text{O}_3^{--}$ ions, a deep violet color results which gradually disappears owing to the formation of Fe^{++} and $\text{S}_4\text{O}_6^{--}$. If a low concn. of Cu^{++} is present the decolorization takes place much more rapidly at room temp. The accelerating effect of 0.0002 mg. of Cu^{++} is noticeable. In the presence of CNS^- , which of itself tends to retard the reaction between Fe^{+++} and $\text{S}_2\text{O}_3^{--}$, the catalytic action of the Cu can be shown very plainly and the Cu content can be estd. by comparing the depth of color with that of a comparison test made with a known

quantity of Cu. The entire decolorization requires 10-20 min. with dil. solns. For carrying out the test the following solns. are recommended: (A) a soln. of 3.9 mg. blue vitriol per l.; (B) 5 g. ferric alum + 25 cc. 2 N HCl diluted to 1 l.; (C) 4 N NH_4CNS soln.; (D) 0.067 N $\text{Na}_2\text{S}_2\text{O}_8$. The test for a trace of Cu^{++} may be made in this way: Place the nearly neutral soln. to be tested in a wide beaker of about 500-cc. capacity. In a series of similar beakers place 0, 0.2, 0.4, 0.6 and 0.8 cc. of the standard Cu soln. and bring all the solns. to the same vol. by diln. with water. Add to each beaker 100 cc. of a $\text{Fe}(\text{CNS})_3$ soln. prepd. by mixing 10-20 cc. of soln. C with 2 l. of soln. B (for larger quantities of Cu, up to 3 mg., use more of this mixt.). Now add 25 cc. of soln. D as rapidly as possible to each beaker and mix. In colorimetric tubes, compare the unknown soln. with that most like it of the standards. The presence of strong acids or any considerable amt. of ions such as those of Al, Zn, Ni and especially As retards the decolorization effect and when these ions are present, the standards should be treated with corresponding quantities.

W. T. H.

The estimation of chromium and iron in chrome residues. KARL SCHORLEMMER. *Collegium* 1922, 247-50; cf. *C. A.* 12, 2506.—The presence of org. matter in Cr residues, especially those from the prepn. of dyes, prevents the oxidation of Cr by H_2O_2 in alk. soln. With KMnO_4 the Cr is oxidized but the Fe is pptd. as $\text{Fe}(\text{OH})_3$. Destruction of the org. matter by ignition leaves the ignited Fe_2O_3 hard to dissolve. The proposed method consists in slowly adding a suitable amt. of $\text{K}_2\text{Cr}_2\text{O}_7$ soln. to the Cr residue dissolved in dil. H_2SO_4 , carefully boiling between each addn. The destruction of org. matter is shown by foaming. When this ceases and the soln. is of pure green color, the soln. is filtered and made up to 500 cc. An aliquot portion of this is then oxidized with H_2O_2 , and Cr and Fe are estd. as usual. The procedure is to be patented.

F. L. SEYMOUR-JONES

Potentiometric titration of copper. E. ZINTL AND H. WATTENBERG. *Ber.* 55B, 3366-70(1922).—Accurate results can be obtained electrometrically by reducing Cu^{++} to Cu^+ with TiCl_3 in HCl soln. and titrating the excess of TiCl_3 with KBrO_3 or $\text{K}_2\text{Cr}_2\text{O}_7$ soln. in an atm. of CO_2 . The reaction is slow at room temp. but is instantaneous at 80° , which is recommended for the final titration. The soln. should contain 4-8% of free HCl and the end point should be taken at the max. change per 0.01 cc. of soln. added. If any Fe is present in the soln. or in the reagents, it is detd. with the Cu. W. T. H.

The carrying down of zinc by copper sulfide. I. M. KOLTHOFF AND J. C. VAN DIJK. *Pharm. Weekblad* 59, 1351-60(1922).—The sensitivity of the ZnS pptn. in acid medium depends not only on the Zn concn. but also on the acid concn. and the temp. In the presence of CuS the pptn. of ZnS is accelerated. For the quant. sepn. of Cu and Zn the H_2S should be passed in during as short a time as possible. From solns. acidified with H_2SO_4 the pptn. should be performed at room temp.; from HCl solns. it is better to ppt. at boiling temp. In both cases the acidity should be at least 0.5 N when other ions are absent and the problem is merely a sepn. of Cu^{++} and Zn^{++} .

A. W. DOX

Notes on the determination of phosphorus. G. E. F. LUNDELL AND J. I. HOFFMAN. *Ind. Eng. Chem.* 15, 44-7, 171-3(1923).—The effect of varying conditions upon the complete pptn. of P as ammonium phosphomolybdate has been studied very carefully with particular reference to the detn. of P in Fe, steel, alloy steel and bronze. Precise directions are given for the accurate analysis of such materials ending with a weighed ppt. of $\text{Mg}_3\text{P}_2\text{O}_7$ and a rapid method is described which is based upon the alkali-metric titration of the yellow molybdate ppt.

W. T. H.

The photochemical detection of silver in ore sections. G. SILBERSTEIN AND E. WEISS. *Z. anorg. allgem. Chem.* 124, 355-6(1922).—In the microscopic study of some ore sections, Ag was detected by treating with satd. KI soln. and getting the typical effect of light upon the film of AgI. In some complex ores, however, the test was ob-

tained only after several hrs. of contact with the KI solu. although the ores were fairly rich in Ag.

W. T. H.

The determination of oxygen in steel. GEORGES CHAUDRON AND LOUIS BLANC. *Compt. rend.* 175, 885-7(1922).—The detn. of O in steel is carried out by heating 5 hrs. in a current of H and absorbing in P_2O_5 the H_2O formed. The operation takes about 5 hrs. In the first 3 hrs. the temp. is allowed to rise to 1000° and subsequently to 1175 – 1200° . A blank run shows that a blank amounting to 0.1 mg. per hr. of heating can occur, thereby introducing a possible error of 0.5 mg. during the entire procedure. The total amt. of O weighed is usually about 5 mg. A part of the O may also escape detn. in the form of CO_2 . Reduction with the addition of alloys of Cu-Sn-Sb causes little difference in the results obtained. In the reduction of fused mixts. of Fe and MnO the alloy method does not permit the reduction of MnO when in greater proportion than 2 parts MnO to 1000 parts of alloy. With fused mixts. of Fe and SiO_2 the amt. of H_2O obtained is not measurable, being within the limits of exptl. error. A. G. S.

Rapid determination of lead in solders. VAN AERDE. *J. pharm. Belg.* 4, 909-10 (1922).—To det. the lead in solders used for sealing tin cans, Van A. proceeds as follows: To about 1 g. of solder in a 60-cc. beaker add 10 cc. of concd. HNO_3 , cover the beaker with a watch glass and allow the reaction to proceed at ordinary temp. with frequent stirring. When the reaction has ceased, remove the watch glass and evap. the soln. to dryness on a water bath. Take up the residue with a few drops of HNO_3 and transfer with the aid of H_2O to a graduated 100-cc. flask; dil. to about 60 cc., add 1-2 g. of $AcONa$ and 25 cc. of $K_2Cr_2O_7$ soln. (29.45 g. $K_2Cr_2O_7$ per l.). Add sufficient H_2O to bring the vol. to 100 cc. and shake the mixt. vigorously. Centrifuge or allow the ppt. to settle and decant the supernatant liquid through glass wool and asbestos. Take 25 cc. of the filtrate in an Erlenmeyer flask, add about 2 g. of KI, 10 cc. of dil. H_2SO_4 and a little H_2O_2 ; titrate with 0.1 N $Na_2S_2O_3$. A. G. DuMEZ.

A micro-method for the determination of sulfur using benzidine. C. ZIMMERLUND AND O. SVANBERG. *Svensk Kem. Tids.* 34, 139-46(1922).—Benzidine hydrochloride reacts with the sulfate ion giving a ppt. which is but slightly sol. One l. of water dissolves 69 mg. benzidine sulfate and 0.01 N HCl dissolves 78.5 mg. The method is reliable for samples carrying from 0.5 to 2.5 mg. S. The app. used are those given in Bang's test on micro-methods. Wash water and reagents must be tested for S. The procedure is: First carefully neutralize the soln. and then add 2 cc. benzidine reagent, shake, filter, wash, and titrate with 0.05 N NaOH, phenolphthalein being used as indicator. For org. compds. weigh the sample into a small special Pt crucible together with 0.2 g. $NaClO_3$ and 8 mg. NaOH (from Na). Place the crucible in a test tube and heat until the contents are well fused. Then dissolve the contents in 0.2 N HCl. Add phenolphthalein and then 0.02 N NaOH until it is distinctly red. Just destroy the red color with 0.01 N HCl. Then add 4 cc. benzidine reagent and proceed as for inorg. sulfate. For the reagent take 2 g. benzidine hydrochloride and shake in 200 cc. water. Filter and titrate. Add to this soln. HCl in such quantities that 1 cc. of the reagent will equal 2.5-3 cc. 0.05 N NaOH. A. ROSE.

Method for the simultaneous determination of sulfur and halogen in organic compounds. C. S. LEONARD. *J. Am. Chem. Soc.* 45, 255-7(1923).—Klason's method has been so simplified, through years of usage in Sweden, that it now surpasses the Carius method and rivals the fusion method in ease, speed and accuracy but it seems to be wholly unknown to American chemists. A combustion tube is drawn out at one end and bent down to dip into 100 cc. of distd. H_2O in a receiver (F). The other end is attached by a fume-treated cork to a bulb (E) of S-free HNO_3 . Dry air or O may be drawn through the acid and the tube. The latter contains, beginning at the drawn-out end, a roll (A) of freshly ignited, fine-meshed Pt gauze, then a porcelain boat (B) filled with fuming

HNO₃, next another roll (C) of Pt gauze and finally a 2nd boat (D) contg. the substance to be analyzed, which is pushed into the tube after the latter has been prepd. by heating the gauzes to dull redness and passing in air to fill the tube with brown fumes. Oxidation of the sample may begin without the application of heat, as shown by the production of white fumes; the heating of the sample and of the boat contg. the fuming HNO₃ must be so regulated that brown fumes are *never* absent behind A but white fumes may be permitted to appear just behind C if a low flame is immediately applied to bulb E (and B is heated somewhat higher, if necessary) to supply more N oxide fumes completely to fill the tube again. The material being analyzed is then driven down the tube by heat (being careful not to heat the tube under B to redness). After the app. has cooled, the boats and gauzes are thoroughly rinsed and finally boiled with H₂O, the tube itself is carefully rinsed out and the washings are combined with the contents of the receiver F. If only S is to be detd. the soln. is heated on the H₂O bath until the odor of HNO₃ has disappeared and the SO₄ ion is pptd. with BaCl₂. If both halogen and S are to be detd. a blackened receiver contg. aq. AgNO₃ is used, the pptd. Ag halide is filtered on a Gooch crucible and washed with 2% HNO₃ and the filtrate freed from the excess of Ag with HCl, then from HNO₃ on the H₂O bath and the SO₄ ion pptd. with BaCl₂. The combustion requires 1.5-2.0 hrs.

C. A. R.

Detection of formalin in organic material, especially in the cadaver. H. LÜHRIG. *Pharm. Zentralhalle* 63, 597-602(1922).—As the result of a toxico-legal case involving the possible ingestion of formalin, a series of expts. was carried out to det. the max. interval (following CH₃O administration) during which the detection of formalin could still be effected. Thus it developed that, contrary to previously accepted views, a positive reaction was obtainable in the case of oatmeal soup over a period of 29 days; of milk 11-31 days, of urine (old and fresh) 8 and 28 days, resp.; beans 8 days, food mixture of honey, sugar, milk, bread, butter and stomach contents of a cadaver 30 days; decomposed blood sausage mass 13 days; human stomach and content (diluted) 39 days; human small intestine and content (undiluted) 27 days. In several of the expts. notably the last two, a positive test was possible only with the undiluted distillate.

W. O. E.

The very sensitive reactions between copper and certain phenols (hydroquinol and α -naphthol). J. ALOY AND A. VALDIGUIÉ. *Bull. soc. chim.* 31, 1176-9(1922).—A dil. soln. of hydroquinol in water tends to become blue if a trace of Cu⁺⁺ is present. The reaction is more rapid at the temp. of boiling water. The development of the blue color is a more sensitive test for Cu⁺⁺ than the blue with NH₄OH or the pink with ferrocyanide. As a reagent for Cu⁺⁺ a soln. contg. 0.2 g. of hydroquinol per 100 cc. of water is recommended and it is important that the soln. to be tested should have a low acidity and that it should not contain any considerable concn. of any salt. The reaction mixt. should be heated to about 100°. A dil. Cu⁺⁺ soln. may be used as a sensitive test for hydroquinol; as little as 0.1 mg. can be detected. With α -naphthol, a dil. Cu⁺⁺ soln. gives a characteristic blue-violet coloration. This color is distinctly different in shade from that produced by hydroquinol and Cu⁺⁺ and the test may be used to distinguish α -naphthol from β -naphthol.

W. T. H.

The quantitative determination of chlorine in benzaldehyde. J. VOIGT. *Z. angew. Chem.* 35, 654-5(1922).—Most synthetic benzaldehyde is obtained by a process which involves the chlorination of toluene and the final product is likely to contain some Cl. Various methods have been described for the detn. of Cl but in all cases it is necessary to decompose the org. matter. An ingenious app. is described in which the substance is volatilized in a stream of H₂ and the gas is burned in another tube contg. O₂. The products of the combustion are passed over anhyd. Na₂CO₃, which absorbs any HCl formed. In this way about 7 g. of benzaldehyde can be burned in an hr. After the

combustion, the Na_2CO_3 absorbent is dissolved in water and the Cl content detd. by titration with AgNO_3 . Very small quantities of Cl can be detd. and it is necessary to run a blank on the H_2 .

W. T. H.

The titration of the alkaloids of cinchona and their salts. N. SCHOORL. *Rec. trav. chim.* **41**, 228-37 (1922).—In order to choose the best indicator for the titration of these alkaloids the course of the neutralization curve in the vicinity of the pts. of equivalence, which corresponds to the formation of the mono- and diacid salts, was detd. This curve can doubtlessly be calcd. for quinine and HCl but detg. the curve is much simpler. These detns. were made in both aq. and 50% EtOH solns. A very pure sample of quinine hydrochloride A ($\text{Q} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$) was recrystd. several times but the tint given to methyl red by a 1/10 mol. soln. remained unchanged at p_H 6.1. The corresponding diacid salt (B) ($\text{Q} \cdot 2\text{HCl} \cdot \frac{1}{3}\text{H}_2\text{O}$) was obtained on evapg. A with the calcd. amt. of HCl. In 1/10 mol. soln. B gives p_H 3.5. The free quinine (C) was also obtained. By mixing A, B and C the neutralization curve in H_2O and 50% EtOH was traced. The p_H of A is in the region of the color change of methyl red and for B it is in the methyl orange region. The titration of C or of the other cinchona alkaloids may be made with 0.1 N HCl using methyl red when considering them as univalent bases or methyl orange when considering them as bivalent bases. The neutralization curve does not pass through the interval of change of these indicators sharply but shows intermediate tints that make the use of comparison liquids necessary when using the diacid salt soln. The titration as a univalent base with methyl red is more precise but the addn. is continued until the tint is nearly completely alk. for methyl red. In practice the alkaloid is dissolved in EtOH and titrated directly with 0.1 N acid or a known excess is added. It is then titrated the other way with 0.1 N alkali. Owing to the fact that the soln. of A is nearly absolutely alk. toward methyl red and nearly absolutely acid toward neutral red the titration of these alkaloids is easily accomplished by making successive use of the 2 indicators. In this titrate as above until the methyl red loses its red color and then add 2 drops of neutral red soln. (1 : 1000 in dil. EtOH) per 10 cc. and titrate with alkali again to the disappearance of the red color. Titration of cinchonine gave the same result. The titration of monoacid salts of these alkaloids (*i. e.*, monohydrochloride) was easily accomplished with 0.1 N HCl and methyl orange but even better with phenolphthalein. The dihydrochlorides were titrated in 2 ways. Methyl red and neutral red can be used successively with 0.1 N alkali in 50% EtOH soln. or phenolphthalein and 0.1 N alkali in 66% EtOH.

E. J. WITZEMANN

Golodet's reaction (reaction for benzoyl peroxide). H. C. J. H. GELISEN. *Rec. trav. chim.* **41**, 224-7 (1922).—Golodet's reaction (*C. A.* **2**, 1672) is sp. for Bz_2O_2 on the one hand and CH_2O on the other. Add 10-12 drops of concd. H_2SO_4 (slightly warmed) to some grains of Bz_2O_2 ; this explodes. The peroxide is decompd. giving white vapors that smell like BzPh or fluoronone. This mixt. treated with a soln. of CH_2O gives a blood-red color which disappears on diln. G. detd. that Golodet's reaction is essentially Hehner's reaction because the red coloration depends on the formation of phenolsulfonic acid. It is not sp. for Ba_2O_2 for many peroxides give explosions in concd. H_2SO_4 and the red color is given by all compds. that give phenolsulfonic acid with concd. H_2SO_4 as *e. g.*, benzoyl acetyl peroxide and phenyl benzoate peroxide. The reactions of Liebermann and Millon for the detection of PhOH are equally applicable to Bz_2O_2 in the conditions of Golodet's reaction. If this reaction is carried out at -20° instead of in warm H_2O it is much more sensitive; the coloration is more intense and the product is not contaminated by tar.

E. J. WITZEMANN

Graphical calculation in the determination of fire damp by the method of the limits of inflammability. C. LECHATELIER. *Rev. ind. minérale* **2**, 371-2 (1922).—The formula for the detn. of the content of fire damp in the air of a mine by the method indicated

by H. LeChatelier is changed to the form $\{1-(x/6)\}\{y/[1-(y/200)]\} = z/[1-(z/200)]$ where x is the content of fire damp sought, y the limit with pure air and z the limit with the mine air. This is then represented nomographically so that by joining the points y and z , a direct reading of x is obtained.

C. C. DAVIS

Determination of combined N in iron and steel (JORDON, SWINDELLS) 9. Determination of glucose, fructose, sucrose and maltose (CAJORI) 11B.

SCHAEFFER, JOHN A. AND WHITE, BERNARD S.: **Chemical Analysis of Lead and Its Compounds**. 2nd Ed. Chicago: The Eagle Picher Lead Co. 160 pp.

Standard Methods of Chemical Analysis. Edited by Wilfred W. Scott assisted by many collaborators. 3rd Ed. Revised and greatly enlarged. New York: D. Van Nostrand Co. 2 Vols. 1567 pp. \$10.00. Reviewed in *J. Franklin Inst.* **194**, 566 (1922).

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

The application of colloid chemistry to mineralogy and petrology. ALEX. SCOTT. *Brit. Assoc. Advancement Sci.* **1922**, 204-44.—This report treats (1) of the general aspects of colloid chem. applicable to mineralogy and petrology: (1) weathering, (2) cementation, (3) adsorption, (4) determination of colloidal character or origin, (5) dendritic structure, (6) anomalous double refraction, (7) igneous rocks. (2) Rocks and minerals which either exist in colloidal form or are derived from colloidal material: (1) metals, (2) sulfur, (3) carbon, (4) silica, (5) agate, (6) bauerite, (7) chert and flint, (8) siliceous sinter, (9) alumina, (10) Mn oxides, (11) Sb oxide, (12) MgO, (13) Sn oxide, (14) Mo oxide, (15) ice, (16) sulfides, (17) silicates of Al, (18) silicates of Fe, (19) zeolites, (20) serpentine group, (21) other silicates, (22) carbonates, (23) sulfates, (24) phosphates, (25) arsenates, (26) antimonates. A very large number of references are given.

JEROME ALEXANDER

Colloid chemistry and mineralogy. F. RINNE. *Kolloid-Z.* **31**, 269-71 (1922).—In a general way R. discusses colloid chemistry in the formation of minerals, and in its relation to the process of crystn.

E. F. H.

Colloidal phosphates. CARL ELSCHNER. *Kolloid-Z.* **31**, 94-6 (1922).—The occurrence and characteristics of 3 different colloidal phosphates are described. (1) This occurs on Washington Island in the South Seas as a clay consisting of $\text{Ca}_3(\text{PO}_4)_2$ with CaHPO_4 and org. material. This was probably formed similarly to guano followed by soln. and deposit of the $\text{Ca}_3(\text{PO}_4)_2$ as a crust on the bottom and banks of a fresh- H_2O lake. This phosphate clay is plastic, shrinks, swells and behaves like a colloid. (2) *Nauruite*, previously described by E. (no reference), was probably formed by the sepn. in the presence of NH_4OH of $\text{Ca}_3(\text{PO}_4)_2$ contg. H_2O from the gel form. The rings are due to infiltration of ferrous salts with subsequent oxidation, and to the fixation of F from sea- H_2O . (3) On a rocky island near Necker Island in Hawaii occurs a colloidal phosphate contg. AlPO_4 66.33, FePO_4 2.52, H_2O 26.10%. It is probably an old gel and differs from similar phosphates by the great clearness of the Liesegang structural lines. It was undoubtedly formed by decompn. of lava by certain guano constituents.

C. C. DAVIS

A new mineral with rare earths as essential constituents. F. HENRICH AND G. HILLER. *Ber.* **55B**, 3013-21 (1922).—This new mineral, *weinschenkite*, was found in the Amberg-Auerbach district of the Bavarian Oberpfalz. Its structure is felted globular or in radiating needles, in thin crusts on limonite. When pure, its color is snow white.

It is sol. in dil. acids, but not in alkalis; and infusible. No As or F was detected. Analysis gave: H_2O 16.42, rare earth oxides (Y and Er chiefly, at. wt. 101.9) 52.47, P_2O_5 30.2, insol. 0.38 , Fe_2O_3 0.24 , sum 99.71% . This gives the formula $(\text{Y}, \text{Er}) \text{PO}_4 + 2\text{H}_2\text{O}$. Another mineral named *pseudo-wavellite*, from the same locality, is a hydrous Al phosphate, with CaO 13, rare earths 2-3, $\text{SrO} + \text{BaO}$ 1% . E. F. H.

Mineralogic notes on pucherite, pyrite, trichalcite and wavellite. E. V. SHANNON. *Proc. U. S. Nat. Museum* 62, 1-10(1922).—Pyrite from Ark. is distinguished by the unsymmetrical development of its crystals. From cuboctahedrons they vary to prismatic, or flattened to moderately thin square tables. Pucherite from Minas Geraes, Brazil (Bi vanadate) shows a new pyramid $k(122)$. Trichalcite from Shoshone Co., Idaho is the first instance of this rare arsenate being found outside of the original locality in the Urals. It was identified by its optical properties. Wavellite from Ark. was first labelled "natrolite on variscite," but was identified by optical measurements by E. S. Larsen and chem. tests. L. W. RIGGS

Hay and Buffalo Rivers, Great Slave Lake and adjacent country. A. E. CAMERON. *Can. Dept. Mines, Summary Report* 1921, Pt. B, 1-44.—Pb, Zn, clays, gypsum and salt occur in this immense region of over 60000 sq. mi. Oil and bituminous matter exist near Great Slave Lake in sufficient amts. to warrant further exploration with the drill. **Mackenzie River District between Great Slave Lake and Simpson.** E. J. WHITTAKER. *Ibid* 45-55.—This report covers a reconnaissance which will be of value in further exploration. **Exploration east of Mackenzie River between Simpson and Wrigley.** M. Y. WILLIAMS. *Ibid* 56-66.—Limestone was found in abundance but the outlook for oil was not promising. **North Nahanni and Root Rivers Area and Caribou Island, Mackenzie River District.** G. S. HUME. *Ibid* 67-78.—Prospect on Caribou island, from some of which Au had been obtained, were examd. but no Au found in the samples taken. As many excavations had been made, the one yielding Au was probably overlooked. **Geological structure of the Mackenzie River Region.** D. B. DOWLING. *Ibid* 79-90.—**Kananaskis Lakes—Palliser River Map-Area.** J. R. MARSHALL. *Ibid* 91-4.—The Kootenay formation, which is described, carries all the workable coal of this district. The coal is the high-C bituminous variety. Analysis of 4 samples gave fixed C (by difference) 70.7 to 78.8%, B. t. u. 12930 to 14930. The outlook for profitable mining is good. L. W. RIGGS

Geology and mineral deposits of the Bridge River Map-Area, British Columbia. W. S. McCANN. *Can. Dept. Mines Geol. Survey, Memoir* 130, 115 pp.(1922).—The area studied lies 125 miles northeast of Vancouver along the line of the Coast Mts. and west of Lillooet. The Au production since 1874 totals \$2,000,000. Arsenopyrite and pyrite occur in large amts., chalcopyrite, galena, sphalerite, stibnite and tetrahedrite sparingly. The outlook for the profitable production of Au by the installation of modern mining methods is fairly promising. Placer deposits have been the chief factor in the prosperity of the province. The Ag-Cu deposits are far removed from good transportation facilities and can be worked but 5 months of the year. A small deposit of Cr was found in this area; a specimen of the ore gave 48.72% Cr_2O_3 . The presence of microscopic diamonds was noted in the chromite. Magnesite, asbestos and a Ni-Fe alloy (contg. Ni 67.93%, Fe 31.02 and Co 0.70) occur in this region. About 20 mines and prospects are described. L. W. RIGGS

The metallogenic provinces of China. WEN-HAO WONG. *Bull. Geol. Survey China* 2, 37-59(1926).—Iron oxides and sulfides occur in contact-metamorphic deposits due to grano-diorite intrusions. Cu sulfides are locally found with those of Fe. There are Au, Fe, Cu, Pb, Zn, W, Mo, and Mg ores, and apatite in the areas of ancient metamorphic rocks. In southern China are zones of Sn minerals with those of W and Mo; Zn, Pb, and Cu; Sb; Hg. The various localities are described. E. F. H.

Report on the geology and mineral resources of northern Anhui. C. C. LIU AND J. C. CHAO. *Bull. Geol. Survey China* 1, 8-11(1919).—The mineral resources of this region include coal (bituminous and anthracite) and Fe ores. E. F. H.

Gems and precious stones in 1921. B. H. STODDARD. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. II, 143-6(preprint No. 23, publ. Sept. 13, 1922).

E. J. C.

The quicksilver deposits of China. F. R. TEGENGRN. *Bull. Geol. Survey China* 2, 1-36(1920).—Chinese Hg deposits occur principally in Kueichow and adjacent part of Szechuan, Hunan, and Yunnan. The ores are found in irregular veins or stockworks in brecciated limestones and shales, or disseminated in such rocks. The minerals of these veins are cinnabar, stibnite, calcite, quartz, pyrite and bitumen, also rarely native Hg and onofrite. Most of the deposits run less than 1% Hg; but locally reach 3-4%. Mining methods are primitive. The cinnabar is reduced by (1) oxidizing the S in air, (2) decompn. of the sulfide in closed vessels by means of CaO or Fe. E. F. H.

The Hsi-Ku'ang-Shan antimony mining fields, Hsin-Hua district, Hunan. F. R. TEGENGRN. *Bull. Geol. Survey China* 3, 1-26(1921).—These, the largest Sb deposits in the world, are located at lat. 27° 48', long. 4° 53', west of Peking. The country rocks are chiefly sandstones and limestones. Stibnite occurs in a quartzitic sandstone, with quartz and secondary Sb oxides. E. F. H.

Antimony mines of Shiu Chow, China. G. D. HUBBARD. *Am. J. Sci.* 4, 453-60 (1922); cf. C. A. 16, 3455.—The geologic features of the region are described. Stibnite and weathered Sb ores have been collected for several years in this locality. In 1920 a body of ores several ft. thick was discovered. The ore varies from pure stibnite to stibnite and calcite gang running from 65% down in Sb. Mining is done by the simplest hand methods and the ore is carried on the backs of peasants 5 miles to the smelters at Shiu Chow. These smelters are simple reverberatory furnaces burning wood and fed by hand. The S goes up the stack with the smoke and the Sb is drawn off into 25 and 200 lb. ingots which find sale in America and England. China is well supplied with Sb, 8 other localities being mentioned. L. W. RIGGS

Iron-bearing rocks of Belcher Islands, Hudson Bay. G. A. YOUNG. Can. Dept. Mines Geol. Survey, *Summary Report 1921*, Pt. E. 61 pp.—Belcher Islands lie off the eastern coast of Hudson Bay 70 miles north of Cape Jones which marks the division between Hudson Bay and James Bay. The av. of 3 fairly representative samples of the ore gave the equiv. of 40% metallic Fe and 42% of SiO₂ which is too high in SiO₂ for profitable smelting. The outcrops indicate a very large total quantity of Fe in this region, but further prospecting is necessary before deciding upon the feasibility of its exploitation. L. W. RIGGS

Brown hematite ores of western North Carolina. W. S. BAYLEY. U. S. Geol. Survey, *Bull.* 735F, 157-208(1922).—The deposits which are of com. importance are located in Cherokee and Madison counties and are associated with Cambrian sedimentary rocks. The ores are mixts. of hard goethite, limonite and soft sandy limonite. In carload lots they run 45 to 50% Fe, 0.25 to 1.25 Mn, 0.3 to 0.7 P, and 8 to 18.0 SiO₂. The S content is rarely more than 0.1%. The ores of the Piedmont Plateau in Gaston county contain 50 to 64% Fe and P not more than 0.08. These deposits are more expensive to operate than those in Cherokee county or in Va. **General features of the magnetite ores of western North Carolina and eastern Tennessee.** *Ibid* 735G, 209-70 (1922).—These ores consist of brown hematite, magnetite, and titaniferous magnetite mixed in various proportions. The compn. of the non-titaniferous ores ranges as follows: SiO₂ 3.2 to 32.6, Fe 36.4 to 65.4, S tr. to 0.2, P 0.004 to 0.06, TiO₂ 0.06 to 0.95, Mn 0.16 to 2.58%. Several mines are described and about 35 chem. analyses of ores are given. L. W. RIGGS

Chromite of Kenai Peninsula, Alaska. A. C. GILL. U. S. Geol. Survey, *Bull.* 742, 50 pp. (1922).—The only chromite mining in Alaska was the production of about 2000 tons in 1917-1918 at Claim Point. The ores are mixts. of chromite and olivine and seem to have been formed by early crystn. from a highly magnesian magma. Fourteen deposits at Port Chatham and 23 at Red Mt. are described, the estd. amts. of ores in sight being 32,300 and 195,600 tons resp. Ability of Alaskan chromite to compete with chromite from other regions depends on miners wages and ocean freight rates. L. W. R.

An attack on the anticlinal theory. ANON. *Petroleum Times* 8, 871 (1922).—Crude oil existed in the earth before the movements which caused formation of anticlines, synclines and domes took place. The lateral migration of oil underground is due not to bouyancy which is too small a force, but to the hydraulic pressure of water.

D. F. BROWN

Brooks, Steen and Grand Saline salt domes, Smith and Van Zandt counties, Texas. SIDNEY POWERS and O. B. HOPKINS. U. S. Geol. Survey, *Bull.* 736G, 179-239 (1922).—Salt domes in the U. S. are confined to the coastal plain in Texas and La. They are abundant in Mexico. A theory of their formation is advanced and brief descriptions of 64 domes are tabulated. The domes mentioned in the title are described at greater length. Logs of wells down to 4000 ft. are given and analyses of several salt samples in which the NaCl ranges from 92.75 to 99.8%. In making further study of this problem it is advised to drill deep and exam. the drillings microscopically. L. W. RIGGS

Salt, sulfur, gypsum. Their relation to hydrocarbons. R. CORTESE. *Rass. min.* 57, 37-40 (1922).—A discussion of the sedimentary formation of NaCl, S and CaSO₄, particularly in Italy. Assuming that NaCl and CaSO₄ were both originally present in terrestrial H₂O, concn. in natural basins resulted in CaSO₄ pptg. first, followed by the more sol. salts, chiefly NaCl. As a result, CaSO₄ deposits should always be older than NaCl and should lie below the latter. According to Mottura (cf. Balducci, *Descrizione geologica dell'Isola di Sicilia*) free S results from the reduction of CaSO₄ by hydrocarbons, thus: $\text{CaSO}_4 + 2\text{C} \longrightarrow \text{CaS} + 2\text{CO}_2$; $\text{CaS} + 2\text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{S} + \text{CaCO}_3 + \text{CO}_2$; $\text{H}_2\text{S} + \text{CaCO}_3 + \text{O} \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{S}$. Correlating these theories, it is necessary that CaSO₄ and S should always occur together. Sp. geologic examples are given to show that this is usually true. But objection is made to this explanation of the presence of S for 3 reasons: (1) though the C is furnished by hydrocarbons, no account is taken of the H of the latter; (2) CaS through its soly. is removed from the sphere of action and with air and H₂O would form cryst. CaSO₄ \longrightarrow and (3) the great deposits of cryst. CaSO₄ formed subsequently to S are not explained. It is contended that the actual geologic formations can be explained differently. Assuming the primary formation of H₂S within the earth's crust from S and infiltrated H₂O, the following sequence of reactions may occur: $n \text{CaCO}_3 + 5n \text{H}_2\text{S} \longrightarrow n \text{CaS} + 3n \text{H}_2\text{O} + 4n \text{S} + n\text{H}_2\text{S} + 2n \text{H}$; $n \text{CaS} + 4n \text{H}_2\text{O} \longrightarrow n \text{CaSO}_4 + 8n \text{H}$; $n \text{CaCO}_3 + n \text{H}_2\text{S} + 4n \text{H} \longrightarrow n \text{CaS} + 3n \text{H}_2\text{O}$. The CaS dissolves in excess H₂O and is removed, whereas the S remains. A certain amt. of CaS is transformed to CaSO₄ and is found present with the S, but the greater part is deposited in cryst. form and not always above the S. In short it is concluded that (1) deposits of salt can occur free of gypsum and if they are accompanied by gypsum, it is by small amts. and in such proportions that the ratio of soly. of CaSO₄ and NaCl is maintained; (2) S results from the action of H₂S and CaCO₃ and it is presumably siliceous limestone which has furnished the necessary material for this reaction. This S is deposited at the location where the reaction between the H₂S and CaCO₃ occurs and (3) the CaS produced is promptly transformed into CaSO₄ and is pptd. with S. These are often sandd by the SiO₂ of the siliceous limestone or by incursion of H₂O carrying alluvial sands or clay. Most of the CaS remaining in soln. is gradually transformed into CaSO₄ and has formed large surplus deposits of cryst. gypsum subsequently to those of S. C. C. DAVIS

Occurrence and uses of peat in the United States. E. K. SOPER AND C. C. OSBORN. U. S. Geol. Survey, *Bull.* 728, 202 pp. (1922).—This report describes the peat deposits of the region lying east of the 97th meridian and east or north of an irregular line extending from Fla. along the Atlantic coast 25 to 50 miles inland to southern N. J. and thence westward to central Iowa. Among the subjects treated with special fullness are: origin of peat, its phys. properties, compn. as shown by about 1000 analyses, uses, the peat industry in the U. S., causes of failure in the industry, marl and other limestone deposits associated with peat, leading deposits in the region and quantity available.

L. W. RIGGS

Eruptive rocks on the border of the Mesozoic and Cenozoic of Algarve and their geologic age. PEREIRA DE SOUSA. *Compt. rend.* 175, 822-4 (1922).—Chem. analyses of 4 samples are given, representing berindrite, porphyric limburgite, and 2 ankaramites. These rocks are described with reference to their lithologic and genetic relations.

L. W. RIGGS

Deccan traps and other plateau basalts. II. S. WASHINGTON. *Bull. Geol. Soc. Am.* 33, 765-803 (1922).—The texture is usually ophitic. Augite and labradorite (about Ab_1An_2) make up 90% of the rock, both being present in nearly equal amts. The hypersthene mol. in the augite is about equal to the diopside mol. This is in strong contrast with basaltic augites from Etna, Stromboli, Vesuvius, and Alban Hills. Magnetite is common but nephelite and olivine are rare constituents. The quantity of augite and Fe_3O_4 diminishes with the increase in the content of glass, indicating that these two are the last to crystallize and that the glass has the compn. of a mixture of augite and Fe_3O_4 . Chemically the plateau basalts show a higher Fe and Ti content than volcanic cone basalts, the latter being relatively high in MgO and CaO. The high Fe content of the plateau basalts explains its fluidity at the time of its extrusion. W. F. HUNT

The hot water supply of the Hot Springs, Arkansas. KIRK BRYAN. *J. Geology* 30, 425-49 (1922).—The mineral content of 46 springs varies from 170 to 310 p. p. m. In only a few instances is it below 270 or above 290. SiO_2 varies from 32.5 to 52.3; Ca 26-50; HCO_3 94-172; SO_4 6-28; Cl 2.36-3.33; small amts. of Mg, K, and Na were found, and traces of B, I, and Br. No evidence of Ra salts was detected, although the intensity of radioactivity varies from 0.5 to 265.8. The temp. measurements range from 95.4 to 147° F. Both the juvenile and meteoric theories for the origin of the hot water are discussed in the light of our present knowledge of the geology of the region, but no definite decision is reached.

W. F. HUNT

Inorganic constituents of marine invertebrates, second edition, revised and enlarged. F. W. CLARKE AND W. C. WHEELER. U. S. Geol. Survey Professional Paper 124, 1-62 (1922); cf. C. A. 11, 1941.—Under new analyses of marine invertebrates are tabulated: foraminifera 7, orbitolites 4, sponges 22, madreporian corals 28, alcyonarian corals 22, hydroids 6, annelids 6, crinoids 24, fossil crinoids 10, sea urchins 14, starfishes 29, ophiurans 17, holothurians 4, bryozoans 13, calcareous brachiopods 5, phosphatic brachiopods 4, pelecypod shells 11, scaphopod 1, amphineuran 1, gastropods 20, cephalopods 3, barnacles 7, crustaceans 13, lobster shells 3, algae 27, and other analyses, making 322 in all. Many older analyses are quoted in the discussion. The presence of large amts. of SiO_2 in organisms other than radiolarians, diatoms and sponges is considered an impurity. Fe beyond a trace and Al are probably impurities from adherent mud. Ca is the dominant inorg. constituent in all but siliceous organisms. Mg is much more widely distributed as an essential constituent of marine invertebrates than has hitherto been supposed. P is abundant in the phosphatic brachiopods, crustaceans and alcyonarians. $CaSO_4$ is generally of minor importance. Many of the metals were present in minute amts., e. g., Cu in oysters.

L. W. R.

The significance of mica minerals as a source of K for plants (GOLDSCHMIDT, JOHNSON) 15. Report of the Tin and Tungsten Research Board (ROSE, *et al.*) 9. Crystallography of SbBr_3 (SLAWSON) 2.

SINGEWALD, JOSEPH T., JR., AND BERRY, E. W.: *The Geology of the Corocoro Copper District of Bolivia*. Baltimore: The Johns Hopkins Press. 115 pp. \$1.25. Reviewed in *Economic Geology* 17, 619(1922).

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

Recent advances in metallurgical chemistry. ELAINE EUSTICE. *Chem. Age* (London) 8, 26-8(1923). E. J. C.

Colloid chemistry and metallurgy. W. D. BANCROFT. *Mining & Met.*, preprint, 1922.—A review, giving reasons for rejecting Beilby's amorphous-film theory, some applications of colloid chem. principles to metallographical data, corrosion, and ore flotation. JEROME ALEXANDER

Fifty-fourth annual review and year book. *Eng. Mining J.-Press* 115, No. 3, 89-168(1923).—This annual review no. contains articles on mining, metallurgy, trade and other industrial information for the various com. metals (Cu, Pb, Zn, Au, Ag, Ra, U, V, Fe, Sb, Mo, Hg, Pt, W, Ni, Al, Cd, Ce, Se, Te, Ti, Tl, Zr and Mn), on petroleum, and on certain economic minerals (asbestos, feldspar, kieselguhr, barytes, borax, magnesite, phosphate rock, nitrate, silica, fluorspar, chromite, talc, S, pyrite, bauxite, graphite and mica). The following are of most chem. interest: "Milling and flotation," by A. F. TAGGART; "Hydrometallurgy," by RUDOLF GAHL; "Pyrometallurgy," by E. H. RONIG; and "Mill design and construction," by ERNEST GAYFORD. E. J. C.

Report of the Tin and Tungsten Research Board. T. K. ROSE, *et al.* *H. M. Stationery Office, London*, 1922, 100 pp.—Researches on Cornish ores, including ore-dressing methods and the chem. recovery of metals by leaching and volatilization. **Tin dressing in Cornwall.** F. H. MITCHELL.—A consideration of methods already in use. The activation of cassiterite (A) by flotation has been unsuccessful. **The microscopic examination of veinstones.** F. H. DAVISON.—The size of A was very variable, with a max. of 1.5 mm. diam. Coarse Sn was often intermingled with fine, and in some dres A averaged under 0.022 mm. One-half of all samples contd. 25% A so fine that dressing would entail considerable losses. All lodes are classified in groups according to their mineral components and structure. The veinstones showed A of more than 1 type of crystn. Pulverizing produced a certain amt. of slime size. Brecciated veinstones consisted of angular capel and quartz (B) fragments cemented by A and B, with sulfides and chlorite (C) absent, but with large tourmaline (D) crystals and a little fluorspar (E). B-C veinstones at higher levels contd. a little D, and A of good size accompanied by sulfides. In Sn-W lodes crystn. was coarse, with wolframite (F), B, C, mispickel and A, and some scheelite, calcite, D and E. The slate is of value, contg. veinlets of B, D and large-sized A. All crushed veinstones contd. considerable A below 20 μ . **The use of the microscope in the study of slime treatment.** H. W. HURCHIN.—The finer A particles, though retained by Rag frames, were lost later in dressing, and Sn concentrates as sold contd. very few fine particles. The direct measurement of particles in slime was impracticable, but a new method was devised which removed all gang (G) and allowed such measurements. The material was fused with KHSO_4 , until clear, dissolved in cold H_2O , acidified with HCl, filtered, the residue washed, treated with $\text{HF} + \text{HCl}$, evapd. to dryness, concd. H_2SO_4 added, evapd. to white fumes, HCl added, dild. and warmed. The ppt. A was filtered off, ignited and weighed. The

effect of the degree of flocculation upon water concentration of slime tin. S. J. TRUSCOTT AND A. YATES.—The attempt was made to effect differential flocculation of A and G. $\text{Ca}(\text{OH})_2$, KMnO_4 , niter cake, H_2SO_4 , $(\text{CO}_2\text{H})_2$, and citric acid had a flocculating action decreasing in this order, MgCl_2 , NaCl , Na salicylate, and gallic acid had no effect, and Na_2CO_3 , tannin and $(\text{CO}_2\text{Na})_2$ inhibited flocculation. Ox-gall below 0.2% was a flocculator but above was a deflocculator. Friability tests. A. YATES.—A was slightly more friable than G contg. B, but ground equally well. Galena (H) and Cu pyrites were much more friable than either. Report of H. S. Hatfield. H. S. HATFIELD.—A study of the sepn. of A and G by means of (1) the elec. charge in H_2O suspension, (2) flocculation, (3) surface energy, (4) metallic cohesion, (5) inertia and (6) differing dielec. consts. Method (1), as applied to clays in general, was unsuccessful. (2) Addn. of soap to the main influx of spitzkasten failed on account of the Sn being too finely divided to be caught. (3) was carried only far enough to prove that A particles, unlike G, were attracted to certain oil globules. Previously reduced ore was blown above the m. p. of Sn on to a Sn surface in a reducing atmosphere, but the A could not be recovered. Air contg. powdered ore was blown against wax in the attempt to catch the A with greater d., but this was only partially successful. Method (6) consisted in suspending the powder in a liquid, the dielec. const. of which is between that of the G and A. The suspension in 1 vol. PhNO_2 + 3 vols. kerosene, passed through multiple sieve a. c. electrodes, deposited A. With ore ground to 200 mesh, the yield was 85%, with 80 mesh, 65%. Sand contg. only 1% Sn gave a 65% yield, where no other known method was effective. The concentrates contd. 26% Sn. The liquid was recovered by distn. *in vacuo*. H and blend may be sepd. by this process. Tungsten recovery by dissolution in caustic soda. H. W. HUTCHIN.—With a product contg. W in a fine state, 90-5% could be obtained as Na_2WO_4 with concd. NaOH . The reaction proceeded at the b. p. of H_2O and heating under pressure was of no advantage. But unsepd. Sn ore was too coarse to yield a high % of sol. W compds. and the Na_2WO_4 was too impure to be saleable. Pptn. by FeSO_4 was unsuccessful. The use of salt cake in connection with the extraction of tungsten. A. M. DRUMMOND.—The use of salt cake or Na_2SO_4 instead of NaOH or Na_2CO_3 was unsuccessful, but addn. of a small % of Na_2CO_3 increased the extn. and the resulting liquor was but slightly alk. With Na_2SO_4 , a 93% extn. was possible. Tungsten recovery by the Oxland reaction. H. W. HUTCHIN.—Ignition of ore with NaHCO_3 , NaCl and K_2SO_4 with and without addn. of MgO as well as with $\text{Na}_2\text{S}_2\text{O}_3$ alone did not give results worthy of large-scale investigation. Purification of crude tungstate of soda. H. W. HUTCHIN.—No ppt. of NaHCO_3 was obtained by satg. crude Na_2CO_3 and Na_2WO_4 solns. with CO_2 , but NaHCO_3 was pptd. from the satd. liquors by addn. of NaCl or NH_4Cl . Pptn. of Na_2WO_4 solns. was insufficient with FeSO_4 . Volatilization of tungsten oxychloride. O. J. STANNARD.—High-grade F, heated with C at 850° , and Cl passed over it at 300° gave WO_2Cl_2 and WOCl_4 and nearly all the H_2WO_4 was recovered from the sublimate by addn. of H_2O . The H_2WO_4 was dense and easily filtered. With low-grade W ores also, nearly all the W was recovered. This process is recommended for sepg. Sn and W in concentrates. Reduction of the original ore with coal gas, producer gas, CO and H at 750° was also complete. By treating a mixt. of ore and C directly without preliminary high temp. reduction, the same results were obtained. The SnO_2 was not attacked. This offers a com. method for obtaining W from F concentrates rich in tin. By mixing ore with S and treating with dry Cl at 200 - 300° , WCl_4 , WO_2Cl_2 , WCl_3 and FeCl_3 were formed. The possibility of the selective chlorination of ores containing tin and tungsten. W. F. GIBBS.—Ores were treated with COCl_2 , CO-Cl mixt. and HCl in an attempt to chlorinate the Sn alone. No marked selective action was obtained with COCl_2 . Encouraging results were obtained with a mixt. of HCl , H and steam. In the reactions (1) $3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl}$

+ H_2 , (2) $\text{SnCl}_2 + 2\text{H}_2\text{O} \longrightarrow \text{SnO}_2 + 2\text{HCl} + \text{H}_2$, the velocity of (1) from left to right increased rapidly with rise in temp. At $750\text{--}800^\circ$ it was almost complete. The velocity of (2) was still considerable at bright red heat. A mixt. of Fe_2O_3 and SnO_2 , exposed at 800° to HCl , H and steam, should chlorinate the SnO_2 and leave the Fe_2O_3 unattacked. This worked with pure oxides by allowing the charge to descend slowly through a rotating inclined SiO_2 tube. The SnCl_2 was carried away by the ascending current. The residue at the bottom was Fe_2O_3 free from Sn . Sn ores did not work successfully. As was removed completely from ores by exposure to moist HCl gas at $80\text{--}90^\circ$. **The treatment of tin ores by the volatilization of tin as chlorides.** THOMAS K. ROSE.—A detn. of the conditions under which Sn ores could be volatilized and condensed by heating with C and NaCl . The finer the ore the more complete the extn. The amt. of NaCl varied with the % Sn ; 5% NaCl was enough for 2% Sn ore, and it was better to mix the NaCl with wet ore and then to dry than to mix NaCl with dry ore. With 10% concentrates HCl was better than NaCl . The coal necessary was approx. the same as NaCl . The best temp. was 750° . An extn. of 95% Sn was obtained with 1 ore. SnCl_2 was recovered by condensing the vapor to liquid in non-porous pipes between 600° and 240° , solidifying at 240° in glass receivers and converting to SnO_2 by H_2SO_4 . Powdered CaO can be used to absorb the SnCl_2 . **Volatilization experiments at the Central Zinc works, Seaton Carew.** J. H. GOODCHILD.—Large-scale expts. prove that fireclay vessels could be used for distg. Sn ore, C and NaCl . The SnCl_2 was caught in cool Fe pipes. CaCl_2 was superior to salt. It caused less fritting, but unlike NaCl an excess was advantageous. The CaCl_2 could be regenerated by CaO from the SnCl_2 and HCl . Anthracite, bituminous coal and charcoal could be used 60 mesh or finer. **The volatilization of tin from concentrates.** J. H. GOODCHILD.—A concentrate contg. a large % Sn had to have a corresponding amt. of Cl added, but if this were done by CaCl_2 or NaCl the process became unworkable. Expts. with charcoal- HCl , charcoal- HCl -sand, CaCl_2 -sand, HCl -sand and charcoal- CaCl_2 indicated that concentrates richer than 10-12% were difficult to treat. Those 10% or less gave extns. of 90-5% when they contd. enough SiO_2 . Extns. of 97-8% were attained, but careful exptg. for each concentrate was requisite. Recovery of HCl was easy by taking up with fresh concentrate. Losses of acid may be made good by small addns. of NaCl . SnO_2 from 10% concentrates by this process should yield pure Sn not requiring refining. C. C. DAVIS

Roasting by the chloridizing-volatilization process applied to some complex minerals. ANON. *Rass. min. met. chem.* 57, 67-9 (1922).—A discussion of the work of Layng and others on the chloride-volatilization process (cf. C. A. 14, 1649; 15, 2814; 16, 890, 1556). C. C. DAVIS

The concentration of minerals by flotation. EDWIN EDSER. *Brit. Assoc. Advancement Sci. 4th Rept.* 1922, 263-327.—Many finely pulverized substances heavier than water float readily upon its surface; e. g., Au , W , Mo , Fe or brass filings, galena, zinc blende, etc. Others do not; e. g., glass, quartz, feldspar, etc. Impurities lowering the surface tension of water cause sinking; e. g., a floating diamond sank when a mere trace of oleic acid touched the water surface. Rule of thumb uses of these principles are, e. g., detection of bile in urine (jaundice) by the fact that powd. S will not float in it (Hay's test), and the expectoration of betel nut saliva by East Indian natives to sink Au in washing. In one flotation the free air-water surface is increased by air bubbles (foam) which are stabilized by cresol, oils, etc. (aeration). The ore is also rendered more floatable by addn. of a greasy substance (paraffin oil) which further stabilizes the froth, while the gang is rendered less floatable by addn. of, e. g., H_2SO_4 . Fine powd. suspended or deflocculated substances will not float, but with sufficient aeration flocculated substances float. Flotation demands, therefore: (1) a frothing agent, (2) a froth stabilizer, (3) a gang modifier. In practice one substance may serve two or more of these purposes.

The amts. generally used per ton of ore are: oils 1-3 lbs.; H_2SO_4 up to 20 lbs.; alkalis, 3-4 lbs. Seventy million tons of ore are treated annually, mostly low grades otherwise worthless. F. considers in detail air films, surfaces of liquids and solids, contact angles, flocculation and deflocculation, frothing or foaming, practice of flotation, and hypotheses advanced to explain flotation.

JEROME ALEXANDER

Concentration of Rossland, B. C. ores. DOUGLAS LAY. *Eng. Mining J.-Press* 114, 1118-24(1922).—A detailed description of the milling practice in the concn. of low-grade chalcopryite and pyrrhotite ores for the recovery of Cu and Au values. Pyrrhotite concentrates are worthless apart from their Au content. This Au in large part is chemically combined and is not further concd. after a clean pyrrhotite is obtained. Storage of ores or concns. in heaps induces oxidation of the pyrrhotite, and even spontaneous ignition. The effect of such heap-roasting is to free the Au and leave it in a condition readily amenable to flotation.

LOUIS JORDAN

The production and uses of ductile tantalum. C. W. BALKE. *Chem. Met. Eng.* 27, 1271-3(1922).

E. H.

Titanium. R. J. ANDERSON. *Bur. of Mines, Repts. of Investigations No. 2406*, 12 pp.(1922).—A general article, with bibliography.

E. J. C.

Secondary metals in 1921. J. P. DUNLOP. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 151-66(preprint No. 16, publ. Oct. 12, 1922).

E. J. C.

Platinum and allied metals in 1921. J. M. HILL. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 143-9(preprint No. 15, publ. Sept. 19, 1922).

E. J. C.

Antimony in 1921. F. C. SCHRADER. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 121-3(preprint No. 13, publ. Sept. 18, 1922).

E. J. C.

Copper in 1921. H. A. C. JENISON. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 235-81(preprint No. 19, publ. Nov. 4, 1922).

E. J. C.

Cobalt, molybdenum, nickel, tantalum, titanium, tungsten, radium, uranium and vanadium in 1921. F. L. HESS. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 207-33(preprint No. 18, publ. Oct. 23, 1922).

E. J. C.

Silver, copper, lead and zinc in the Central States in 1921. J. P. DUNLOP AND F. BEGEMAN. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 75-105(preprint No. 11, publ. Aug. 15, 1922).

E. J. C.

Gold, silver, copper, lead and zinc in California and Oregon in 1921. C. G. YALR. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 167-206(preprint No. 17, publ. Oct. 23, 1922).

E. J. C.

Gold, silver, copper, lead and zinc in Utah in 1921. V. C. HEIKES. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Part I, 341-62(preprint No. 22, publ. Nov. 27, 1922).

E. H.

Gold, silver, copper, lead and zinc in Arizona in 1921. V. C. HEIKES. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 311-39(preprint No. 21, publ. Nov. 28, 1922).

E. J. C.

Gold, silver, copper, lead and zinc in Montana in 1921. C. N. GERRY. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 283-309(preprint No. 20, publ. Nov. 17, 1922).

E. J. C.

Gold, silver, copper, and lead in South Dakota and Wyoming in 1921. *Mines report.* C. W. HENDERSON. *U. S. Geol. Survey, Mineral Resources of U. S. 1921*, Pt. I, 363-8(preprint No. 23, publ. Dec. 13, 1922).

E. J. C.

Bureau of Mines investigate gold in oil shales and its possible recovery. THOMAS VARLEY. *Bur. of Mines, Repts. of Investigations No. 2413*, 10 pp.(1922).—Au in oil shales can be detd. accurately by an accepted fire-assay method. Only a small percentage of the total Au is recovered by cyanidation and chlorination treatment, which would therefore not be feasible commercially even in the presence of com. quantities.

In the samples of shale examd. the Au assayed no more than 50 cents a ton, and is of no com. value.

G. R. FONDA

Production of iron and steel directly from the ore. RALPH WHITEFIELD. *Iron Coal Trades Rev.* 106, 6-7(1923); cf. *C. A.* 16, 1200, 3053.—A further exposition of the *Bourcoud* process in which is emphasized the generation of a suitable reducing gas high in CO at a temp. of about 1000° so that reduction of the Fe_2O_3 can be effected without the further application of heat. To obtain the requisite intimate mixt. of air and fuel, the latter is pulverized and the air is preheated to 400-800°, the combustion of the C in the heated air ensuring the practically immediate formation of CO_2 . By permitting a regulated amt. of excess C to pass the combustion zone and by causing the mixt. of heated CO_2 and C to traverse the passages of a horizontal cylindrical flue of sufficient length and cross-sectional area, the necessary period of contact of CO_2 and C is obtained, whereby the whole of the CO_2 is converted to CO. The reductive effect of this gas upon the Fe_2O_3 of the ore charge in the rotary reduction furnace, provided with spirals to increase the contact between gas and ore; is to produce a material leaving the furnace consisting of about 80% sponge Fe, 3% Fe_2O_3 , and the rest the unchanged slag-forming materials. The reduced material, which in itself furnishes about 50% of the total heat energy required for the smelting, is finished in an elec. furnace. It is calcd. that, in comparison with standard practice, ingot steel can be produced by this method with 65% of the capital outlay and at 80% of the cost. The process will guarantee the production of the best quality and uniformity of product especially applicable to the most stringent requirements of the engineering industry. J. L. W.

New type of open-hearth furnace. ANON. *Iron Age* 110, 1677-9(1922).—The Loftus furnace is described. The novelty is in the method of application of the blow-torch principle. E. H.

The thermal efficiency and heat balance of an open-hearth furnace. C. L. KINNEY, JR. AND G. R. McDERMOTT. *Blast Furnace and Steel Plant* 10, 629-36(1922).—A test on an open-hearth furnace at South Works, Ill. Steel Co. showed a heat distribution of: (1) CO in waste gases 10.0%, (2) radiation from checkers 7.3%, (3) cooling water 13.5%, (4) gas valve 2.0%, (5) utilized in hearth 16.1%, (6) in waste gases to boilers 51.0%. The heat recovered in the boilers after deducting the steam for blowing the producers was 16.4% of the heat in the coal. New checkerwork construction has decreased the coal consumption from 750 lb. per ton of ingots in 1912 to 596 lb. in 1922. A 100-ton furnace designed on the basis of the test is described. C. H. HERTV, JR.

Use of explosives for loosening blast-furnace charges. PIERRE GALLER. *Rev. métal.* 19, 626-30(Abs.)(1922).—The use of high explosive (TNT 30%, $\text{Pb}(\text{NO}_3)_2$ 70%) in charges of 3-4 kg. is recommended to break up jams in blast furnaces. Details of operation are given. A. P. C.

Changes in grain size with casting sand. R. L. DOTY. *Foundry* 50, 987-9, 996(1922).—Molding sand, carefully sized and measured, was mixed with fireclay under definite conditions and used for a series of runs. To the old sand new sand and clay were added in known amts. The size of grain was then detd. after each batch had been used, and it was proved that the actual size of the particles increased, because of the adhesion of clay to sand. Tables, graphs and illustrations are appended. W. C. EBAUGH

Cast iron grinding tests. A. W. FORBES. *Foundry* 50, 996(1922).—Tests on 4 grinding wheels of Si carbide and one of an alumina abrasive for grinding cast iron, indicated a cost of \$0.30 per lb. for alumina grinding, as against \$0.33 to \$0.54 for the other abrasive. W. C. EBAUGH

Metallographic investigation of different shear cuts. O. BAUER AND O. VOGEL. *Mitl. Materialprüfungsamt.* 39, 53-7(1921).—Pieces 2.5 m. long and 8-25 mm. thick were sheared from annealed and cold-rolled Thomas and Siemens-Martin iron sheets,

with hydraulic and elec. shears. Cold working is greatest with the hydraulic shear and frequent resharpening of the blade is necessary to prevent tearing and slight remelting of the material, especially the cold-rolled sheet. The cuts made with the elec. shear were smooth and only slightly torn. No photomicrographs are given.

W. A. MUDGE

Gases in metals. I. The determination of combined nitrogen in iron and steel and the change in form of nitrogen by heat treatment. LOUIS JORDAN AND F. E. SWINDELLS. *Bur. Standards, Sci. Papers* No. 457, 499-511; *Chem. Met. Eng.* 27, 1135-6(1922).—The N in Fe and steel detd. by the Allen acid-soln. method is that present as nitrides, probably of Fe, Mn, Al, and Ti. Soln. of the metal sample without loss of N may be carried out in a covered beaker. Block-tin condenser tubes are preferred to glass tubes in the NH_3 distn. NH_3 in the distillate is detd. by collection in 0.01 N H_2SO_4 and titration of excess acid with 0.01 N NaOH. The use of Nessler soln. for this detn. gives erroneous results with Fe alloys contg. 0.2% C or over. Certain heat treatments increased the nitride N in an elec.-furnace steel but not in an open-hearth steel of identical compn. Similar increases were observed in a plain C steel and in a series of pure Fe ingots. These data are evidence of the presence in certain steels of 2 forms of N, and of the conversion of free N to nitride N by heat treatment.

LOUIS JORDAN

Two forms of nitrogen in steel. LOUIS JORDAN AND F. E. SWINDELLS. *Chem. Met. Eng.* 27, 1170-1(1922).—See preceding abstr.

LOUIS JORDAN

Fatigue of metals. III. L. BAIRSTOW. *Beama* 12, 811(1922); cf. *C. A.* 17, 523.—The history of a fatigue test, as revealed by an extensometer is developed. Mild steel is subjected to 30,000 reversals of stress, covering a period of 10 days, the stresses varying from ± 14.1 to ± 20.2 tons per sq. in. The "cyclical permanent set" of the metal is shown by curves, including one displaying characteristic features of hysteresis loop produced by fatigue. With non-reversible stresses, e. g., from 0 to +20, the upper limit was found to be much greater. The slipping in crystals and the extension of a specimen depends upon the type of stress to which it has been subjected. A summary of the most striking points in the development of the technic in modern tests and appliances, is offered.

A. H. DICK

Recent researches on the elastic limit. H. A. HOLZ. *Trans. Am. Soc. Steel Treating* 3, 367-85(1923).—A review of various types of app. for detg. proportional limit, elastic limit, and yield point, pointing out the importance and fallacies in the use of these properties in structural engineering design. The practice of European engineers is briefly outlined. A detailed description with photographs of the latest type of Martens extensometer, together with stress-strain diagrams of various ferrous and non-ferrous metals, is given. The instrument may be used with specimens heated to 850° . It operates on a principle similar to a mirror galvanometer, in which the beam of light reflected by the mirror traces a path on a photographic plate. This principle eliminates pencil friction and gives results which permit a study of certain peculiarities in the stress-strain diagrams obscured in those diagrams plotted by earlier instruments. W. A. M.

A metallographic study of hollow rock drill steel as influenced by the method of manufacture. N. B. HOFFMAN. *Trans. Am. Soc. Steel Treating* 3, 436-46(1923).—H. believes that V steel will eventually replace C steel because of greater adaptability to heat treatment. Lab. and field tests, using a No. 248 Ingersoll-Rand drill with 3- and 4-ft. drills, show that the V steels contg. 0.20% V have a life over 3 times as long as the C steels of equal C content (0.75-0.90%). The tests were followed closely by microscopic examn., the results of which are given in several photomicrographs.

W. A. MUDGE

The heat treatment of cast steel for hydroelectric power machinery. B. ECKBERG.

Trans. Am. Soc. Steel Treating 3, 422-9(1923).—An outline of specifications usually used in ordering steel castings for hydroelectric power production in Norway, including chem. compn., phys. properties, and heat treatment. A heat treatment is given which brings the impact figure nearly up to the toughness for a 4.00% Ni, 1.00% Cr elec. steel contg. 0.20% C.

W. A. MUDGE

The characteristic curves of a nickel steel and a chrome steel. H. JUNGBLUTH. *Stahl u. Eisen* 42, 1392(1922).—The hardness obtained in a nickel or chrome steel depends on the temp. of quenching and the rate of quenching. Further there is a curve of a max. hardness which can only be obtained by certain combinations of quenching temp. and rate. If the steel is quenched from a higher temp. it is softer because of the presence of austenite; if from a lower temp. it is softer because of pearlite formation. For every steel a set of curves of equal hardness may be drawn with rate of cooling and quenching temp. as coordinates. These are the so-called characteristic curves for the steel. They are given for a steel of 0.5% C, 5.0% Ni and for a steel of 1.6% C, 1.6% Cr.

R. S. DEAN

Hardening and tensile strength. The mechanics of the tensile test with plastic metals. FRIEDRICH KÖRBER. *Stahl u. Eisen* 42, 365-70(1922).—With large deformations the increase of true tension is proportional to the reduction in cross section, q . The true tensile strength σ_{max} is given by the equation:

$$\sigma_{max} = \left(\frac{\sigma_0' + 100\alpha}{2} \right)^2 \cdot \frac{1}{100\alpha}$$

Where σ_0' and α are detd. from the linear portion of the $\sigma' - q$ curve. σ_0' is the tension at which reduction in area begins and 100α is the increase from σ_0' to the value of σ' where by extrapolation $q = 100\%$. In breaking under tension the gliding takes place along less and less favorable planes till finally the flow limit is reached; the decrease in cross section is then proportional to the further tension applied. During further deformation the gliding planes so orient themselves as to offer max. resistance to displacement and the metal becomes fibrous, only breaking when the cohesion of the metal itself is overcome. This fibrous condition of hard-drawn wire is evident from X-ray interference diagrams, where the interference lines are not continuous across the film but show light and dark portions.

R. S. DEAN

Segregation phenomena. O. BAUER AND H. ARNDT. *Mill. Materialprüfungsamt* 39, 79-101(1921).—A study of segregation in steel and non-ferrous alloys as influenced by the rate of cooling. Segregation is least where the time in passing from liquidus to solidus is longest; rapid cooling shows 5-15% variation in compn.; the Cu-Mn alloys give the best illustration. The Hg-Pb, Cu-Ni, and Cu-Zn alloys show no segregation on rapid cooling. Diagrams and detailed analyses are given for the following alloys: Cu-Sn (8% Sn), Cu-Mn (28, 84 and 90% Cu), Cu-Ni (25% Ni), Cu-Ag (10% Cu), Cu-Zn (24, 28, and 37% Zn), and Cu-Al (1 and 3.5% Cu), Hg-Pb (25% Hg), Al-Zn (1 and 18% Zn), Au-Ag (20% Ag), and FeC (0.30% C). Cf. C. A. 17, 49. W. A. M.

Carbide segregation in high-speed steel. A. E. WHITE. *Trans. Am. Soc. Steel Treating* 3, 386-92(1923).—The degree of segregation in high-speed steel depends upon the pouring temp., rate of cooling of the ingot, and degree of mech. reduction in the mills. Photomicrographs are given which show typical structures for these operations. The useful life of a tool steel depends upon the proper form of cutting edge, rate of speed, feed at which the work or tool is moving, and proper lubrication, quite as much as the compn. and heat treatment.

W. A. MUDGE

Gas useful in heat-treating room. J. W. SMITH. *Trans. Am. Soc. Steel Treating* 3, 396-414(1923).—A discussion illustrated with many photographs, of the practical application of city or manufd. gas in the heat-treating room, together with the necessary burner and furnace design and equipment for economical service. Gas is clean, easily

handled, and convenient, and, with proper equipment, compares favorably with other types of fuel. W. A. MUDGE

Electrical and magnetic weld testing as applied to butt-welded steel plates. T. SPOONER AND I. F. KINNARD. *Proc. Am. Soc. Testing Materials* 22, Pt. II, 177-86 (1922). E. J. C.

The requirements for riveting sheet and the brittleness of ingot iron due to heating in contact with punched materials. RICHARD BAUMANN. *Stahl u. Eisen* 42, 1865-8 (1922).—Fractures occurring in sheets during hot riveting, especially if the holes were punched, are due to an excessive hammering force which produces severe strains in the metal at a temp. where ductility is low. Care must be taken to have a sheet of good surface and to prevent tearing on punching. An increase in temp. in the sheet of 500° often results; under these conditions 6500-8000 kg. per sq. cm. of rivet cross section are recommended for good results. W. A. MUDGE

The recrystallization of technical iron. P. OBERHOFFER AND H. JUNGBLUTH. *Stahl u. Eisen* 42, 1513(1922).—The observations of Pomp and Sherry are confirmed that in technical iron as distinct from electrolytic iron there is a sharp max. of crystal growth at 10% deformation. The effect of C, Si, Mn and P are studied. No connection is found between pearlite structure and recrystn. R. S. DEAN

Examination of a bronze wheel manufactured 600 B. C. O. BAUER, E. WETZEL, AND O. VOGEL. *Mitt. Materialprüfungsamt* 39, 57-65(1921).—An illustrated description of a well preserved wheel and a corroded extra hub discovered in 1919. The wheel was covered with a dense, bright green oxide and showed evidence of having been welded at one place on the felly and on one spoke. No detailed examn. was made. The extra hub showed fractures characteristic of non-homogeneous, porous, and poorly deoxidized bronze. Corrosion products contained Cu 80, Sn 10.5, and O 8.0%. W. A. M.

Improvement of emery papers. CARL BENEDICKS AND ERIK SÖRBERG. *Z. Metallkunde* 14, 397-9(1922).—Ordinary fine-sized emery paper is fastened to a coarse book-binding paper under pressure so as to provide furrows which will care for the sepd. emery particles and prevent excessive scratching. Photomicrographs show steel samples polished with ordinary and improved paper. W. A. MUDGE

Alterations and corrosions observed in cast-iron water mains. A. A. BADO AND V. J. BERNAOLA. *Anales asoc. quim. Argentina* 10, 168-77(1922).—Analyses of the mixt. of oxides filling pits in cast-Fe water mains at points corroded by electrolysis, and of the Fe itself, showed that all the constituents of the Fe were oxidized except the C. L. E. GILSON

Progress in metal-spraying processes for chemical purposes. R. HOPFELT. *Chem.-Ztg.* 47, 33-4(1923). E. H.

Influence of phosphorus on brasses. A. PORTEVIN. *Technique moderne* 14, 510-1(1922).—Two sets of brasses with increasing P contents were prepd., the first contg. an av. of 68% Cu (with a single constituent α), the second with about 58% Cu (with two constituents α and β'). The brasses were cast in metal molds as bars 44 mm. in diam., and also in sand. Each casting was tested for tensile strength, hardness, and shock, and was examd. micrographically. The physical tests show that the mechanical properties are not appreciably affected as long as the P content remains below 0.05%; but when it exceeds 0.5% the elasticity and elongation decrease considerably; the alloys become brittle and harder. The decrease in elongation renders meaningless the values obtained for the tensile strength and the elastic limit. Micrographic examn. gave the following results: A new constituent appears when the P content exceeds 0.05% for α -brasses contg. 68% Cu and 0.5% for ($\alpha + \beta'$)-brasses contg. 58% Cu, which contents are evidently the approx. lower limits of soly. of solid P under the cooling conditions of the tests. The constituent is not readily colored by acid FeCl₃ after

boiling with NaOH and H_2O_2 . It is probably Cu_3P . α -Brass with high P content has the characteristic appearance of the Cu- Cu_3P eutectic of Cu-P alloys. The sepn. of Cu_3P is not appreciably affected by the rate of cooling within the limits of the expts. The addition of P to $(\alpha + \beta')$ -brasses apparently does not appreciably affect the proportions of α and β' ; so that the coeff. of equivalence of brasses with 68% Cu should be approx. 1. The results of the physical tests confirm the unreliability of the results of tensile-strength tests of metals or alloys having but slight deformation under breaking loads, and the absolute necessity of using test pieces cast as part of the castings being tested. The function of P and of deoxidizers in general is briefly discussed. A. P. C.

The relation between the color and the structure of alloys. MASUMI CHIKASAGE. *Z. anorg. allgem. Chem.* **124**, 335-8(1921).—Cu reflects red to orange-yellow light. On the addn. of Sn the alloys become whiter; their whiteness reaches a max. at Cu_5Sn , then falls off because the Sn itself reflects almost only red to reddish blue light. The intensity of reflection depends upon hardness and ability of alloys to take a high polish.

W. A. MUDGE

The relation between the equilibrium diagram and the hardness in binary alloys. TOMIMATU USIHARA. *Sci. Repts. Tohoku Imp. Univ.* **11**, 207-22.—The Shore hardness was tested for various alloys of Cu-Ni, Cu-Fe, Cu-Al, Cu-Sn, Al-Zn, with different heat treatments. *Conclusions:* (1) Insofar as binary alloys form solid solns. quenching affects the hardness but little, since it causes no change in the compn. of any phase. The hardness is a max. for an equal at. ratio of the 2 metals, according to Tammann's theory. (2) There is a change when the quenching temp. passes a eutectoid point or soly. line. (3) The hardness of an annealed eutectoid alloy is a max. compared with neighboring concns. (4) A little aging after quenching is generally observable where eutectoid is present. (5) In Al-Cu alloys quenching from above the eutectic point leaves less hardness than annealing. This directly contradicts the "interference theory" as applied to solid solns. (6) Between hardness and the equil. diagram there is a close relation; hence the hardness may decide doubtful points regarding the diagram.

W. P. WHITE

A list of alloys. WM. CAMPBELL. *Proc. Am. Soc. Testing Materials* **22**, Pt. I, 213-42(1922).—A long list of alloys, primarily non-ferrous alloys, given by common or commercial name, and grouped as brasses, bronzes, Al alloys, resistance alloys, etc. The compn. of each is given.

E. J. C.

Aluminium alloys and their use in castings. ANON. *Raw Material* **6**, 24-34 (1923).—"A complete survey of the various Al alloys with the exception of the Si alloys which have become commercially important relatively recently."

E. J. C.

Binary lead alloys. J. GOEBEL. *Z. Metallkunde* **14**, 388-94, 425-32(1922); cf. *C. A.* **17**, 52.—Alloys contg. 0.80-9.80% Na were studied. The limit of the solid soln. is 0.80% Na; Na_2Pb_3 is formed at 4% Na and 320° ; and NaPb at 9.8% Na and 365° . The eutectic occurs at 6.2% Na and 310° . The sp. gr. of the cast alloys (0-1.6% Na) is slightly greater than that of the slowly cooled alloys. In general slow cooling increases hardness 10 to 30%. The hardness curve rises sharply to a max. at 2% Na, recedes slowly to a minimum at 4% Na (Na_2Pb_3), rises to a second max. at 6.2% Na and falls off again to the minimum at 9.8% Na. With the 0.55% Na alloy and a quenching temp. of $100-310^\circ$ hardness is increased 10-15% on standing 24 hrs. Corrosion increases with percent Na. Only alloys contg. less than 0.78% Na are commercially important.

W. A. MUDGE

Magnetic analysis as a means of studying the structure of iron alloys. K. HONDA. *J. Iron and Steel Inst.* **98**, 375-417, 418-9(1918); *Science Abstracts* **23A**, 167.

H. G.

Alloys. A. DE W. MULLIGAN. *Brit.* **185**, 012, Aug. 22, 1921. Fusible alloys

melting at 155–320° F., particularly applicable for making fuse rods or blocks for use in temp. indicators for bearings, comprize Sb 0.8–2.5, Sn 12–29.6, Pb 12–61, Cd 6.6–18, and Bi 3–15%. The proportion of Sb to Sn is preferably of the order of 1–12. The Sn and Sb are first alloyed, this alloy being then cooled and remelted, the Pb, Cd, and Bi being added successively thereafter.

Ore flotation. H. E. FREDRICK. U. S. 1,438,435, Dec. 12. Acridine or one of its salts or derivs. is used as a flotation agent in the sepn. of ores such as sulfide ores of Cu. U. S. 1,438,436 relates to the similar use of PhOH or cresol together with quinoline or pyridine as flotation agents with either acid or basic ore pulps.

Mineral flotation. C. N. FORREST. U. S. 1,438,590, Dec. 12. A liquid hydrocarbon mixt. obtained from the destructive distn. of gilsonite and rich in unsatd. compds. is used as a flotation agent in aerating aq. ore or slime mixts.

Flotation reagent. J. H. JAMES. U. S. 1,439,107, Dec. 19. A mixt. contg. aldehyde acids such as obtained by oxidation of Cal. petroleum is used to promote the flotation sepn. of Cu pyrites or other ores.

Concentration of ores. S. TUCKER and E. EDSER. Can. 227,193, Dec. 12, 1922. Oil which has been treated with an alkali sulfide is added to the ore pulp as a mineral frothing agent and a froth is formed by bringing gaseous bubbles into contact with the pulp.

Leaching copper ores. H. B. SLATER. U. S. 1,438,869, Dec. 12. Sulfide Cu ore is treated with an excess of an acid leaching agent, *e. g.*, dil. H₂SO₄, and then treated with a hypochlorite to effect further extn.

Porous slag in a dry state. C. H. SCHOL. Can. 227,187, Dec. 12, 1922. Porous, voluminous lumps of slag are obtained by preventing a glassy incrustation by bringing the slag into the granulating water at the height of the water level, the water having as high a temp. as possible at the point where the slag is introduced. The dry frothy slag floating on the water and the wet granulations which sink in the water are recovered separately. App. is also specified.

Concentration of metallic values of ores. W. H. DYSON and L. AIRCHISON. Can. 227,200 Dec. 19, 1922. A metal of the W group is sepd. from materials contg. it in an oxidized form by heating the material in the dry way in an atm. of Cl to effect the volatilization of the metal as a chloride.

Separation of metals. S. GIERSTEN. Can. 225,960, Nov. 14, 1922. Cu is sepd. from Cu-Ni solns. by treating the solns. with bessemerized Cu-Ni mat.

Smelting tin and other ores. JAS. H. GRAY. Can. 226,050, Nov. 14, 1922. A furnace for smelting ores of metals of low volatility has electrodes depending through the roof, a central well contg. resistant material and an annular hearth for the charge.

Treatment of copper-nickel mat. G. HAGLUND. Can. 226,153, Nov. 21, 1922. Cu-Ni mat is converted until the main part of the Ni has been changed to the metallic state, a portion of the mat is treated with acid under access of air and the Cu from the soln. so obtained is cemented out on another portion of the mat.

Conversion of zinc powder into fluid zinc. E. S. BERGLUND. Can. 226,928, Dec. 12, 1922. A condenser has stirring members mounted on horizontal shafts and carrying vanes for stirring the powder.

Conversion of zinc powder into fluid zinc. E. S. BERGLUND. Can. 226,929, Dec. 12, 1922. Zn powder is subjected to centrifugal action, and a stirring operation to sep. the metal drops therefrom. App. is also specified.

Recovering zinc from slag or scoria. K. S. GUITERMAN. U. S. 1,438,643, Dec. 12. Primary slags or scoria-contg. Zn and Fe are smelted with reducing and Fe-replacing materials such as coke and CaCO₃ to form secondary slag substantially free from Fe, from which the Zn is more readily recovered.

Open-hearth furnaces. G. L. DANFORTH, JR. Can. 225,968, Nov. 14, 1922. Means are adjustably introduced through the roof of the furnace and adapted to vary the effective passage area between the ports and melting chamber. Cf. C. A. 17, 55.

Open-hearth port design. G. L. DANFORTH, JR. Can. 225,967, Nov. 14, 1922. Discharge passages for the products of combustion connect the melting chamber and air uptakes and means are provided to prevent flow of air through the discharge passages on the incoming end of the furnace. Cf. C. A. 17, 55.

Melting and refining metals. WM. E. MOORE. Can. 224,263, Oct. 3, 1922. Cold metal is preheated as it is being fed to an elec. furnace, melted in the furnace and maintained in molten condition in the presence of an oxidizing slag to eliminate P, S and C. The temp. is increased in the presence of a deoxidizing slag to eliminate S and desired alloys may be added to the charge during agitation. The furnace structure is also specified.

Heating and stirring the metal in furnace pools. J. R. WYATT. Can. 226,039, Nov. 14, 1922. The molten pool in a furnace is stirred by the hydrodynamic effect of induced elec. currents by setting up whirls of hotter metal entering the pool at two points about the perimeter of the pool and withdrawing relatively cooler metal from the pool along the inside of the hotter metal path.

Tilting oil-fired crucible furnace adapted for melting metals. J. A. GASKILL. U. S. 1,439,409, Dec. 19.

Uniting stellite to inferior metal. T. R. HANCOCK and L. J. HANCOCK. U. S. 1,438,375, Dec. 12. Stellite is used for the tips or edges of high-speed cutting tools by employing Cu or low-fusion cast Fe (having a m. p. intermediate between that of the stellite and the metal forming the main body of the article) as a welding agent.

Oxidizing bright ferrous surfaces. T. RONDELLI and Q. SESTINI. U. S. 1,439,447, Dec. 19. Bright surfaces of ferrous articles are oxidized by simple immersion in an alk. bath contg. a metal electronegative to Fe, e. g., a hot soln. formed of NaOH and PbO, with or without a small amt. of a nitrate or cyanide.

Wrought iron. E. E. ELLIOTT. Can. 226,748, Dec. 5, 1922. A charge of cast Fe, iron ore, purple ore and top-cinder is heated in a special Fe receptacle which may be withdrawn from the furnace and hammered and worked in any desired way.

Pudding iron. E. L. FORD. Can. 225,838, Nov. 14, 1922. The puddle bath is cooled before the beginning of the boiling period by the addn. of FeO to the point where the Fe granulates; the C is then removed and the Fe balled. Cf. C. A. 16, 1737.

Purifying molten alloys with magnesium. F. L. DRIVER, JR. U. S. 1,437,405, Dec. 5. An alloy of Mg with about an equal amt. of a heavier metal such as Ni or Co is added to molten alloys, e. g., Ni alloys contg. Fe and Cr, to effect their purification. The Ni or Co moderates the reaction of the Mg and prevents its flotation and loss.

Reverberatory furnace (for melting copper alloys). W. F. SKLENAR. U. S. 1,438,342, Dec. 12.

Solder for aluminium and its alloys. G. FERRIERE and S. PFYFFER. U. S. 1,437,341, Dec. 5. Sn 85-95, Zn 0.5-9.5, Ag 0.5-4.5 and Cu 0.5-4.5%. Bi, Cd or Pb may also be included in similar solders.

Utilizing liquefied gases in autogenous welding and cutting. W. LACHMANN. Can. 227,183, Dec. 12, 1922. The app. specified has an auxiliary vessel for liquid gas comprising a double-walled vessel with the space between the walls evacuated so as to reduce spontaneous evapn. of the liquid gas to the smallest possible magnitude.

10—ORGANIC CHEMISTRY

CHAS. A. ROULLER

Influence of the structure of organic compounds upon their oxidation with sulfuric acid-dichromate mixture. L. J. SIMON. *Compt. rend.* 175, 1070-2(1922); cf. *C. A.* 16, 3282.—S. suggests the use of $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ oxidizing mixt. in detg. the difference in structure of org. compds. He thinks it may be used in the study of tautomerism and mol. migration. A table gives data on both methods applied to several series of compds.

R. CHESTER ROBERTS

Polar and non-polar valency and organic compounds. W. E. GARNER. *Nature* 110, 543-4(1922).—There are 2 explanations of the positive and negative relationships in org. compds.: (1) there may be a partial transference of an electron between the group and the residue of the mol., or (2) there may be a varying concn. of polar mols. in the typically non-polar compd. It is contended that the second is more likely to be true. An equil. is assumed to exist between the polar and non-polar compds. and this is influenced by the temp., the solvent, etc. Thus, for the org. compd. AX, the equation $\text{AX} \rightleftharpoons \text{AX}^+ \rightleftharpoons \text{AX}^-$ represents this kind of equil.; the more electronegative the group X, the more this reaction proceeds to the right. In those compds. where the stability of the non-polar arrangement is very great, the occurrence of both forms AX^+ and AX^- is possible, and in the presence of a suitable solvent these may give rise to their resp. ions. This view agrees with the occurrence of a group in some compds. with an electropositive, and in others with an electronegative tendency. The ease of replacement of the group X by another group is detd. by the concns. of the polar body, the polar state being the active form of the compd. These concns. may be so small as to escape the ordinary methods of measurement, yet be sufficiently great to explain the velocity of the chem. action.

C. C. DAVIS

Preparation of pure trimethylene. M. TRAUTZ AND K. WINKLER. *J. prakt. Chem.* 104, 37-43(1922).—An app. has been devised for simultaneous prepn., liquefaction, and purification of trimethylene. Its vapor density has been measured in a similarly useful app. as 1.45-1.49, $b_{750} = 34.5^\circ$, $d_{75} 0.720$, $n_D = 1.27^\circ$, n for He light 1.000977 (calcd. 1.000647).

O. B. HELFRICH

Preparation of pure propylene. M. TRAUTZ AND K. WINKLER. *J. prakt. Chem.* 104, 44-52(1922).—An app. is described for the catalytic prepn. of propylene from $\text{MeCH}_2\text{CH}_2\text{OH}$ or better Me_2CHOH and another app. for the purification of the same. It $b_{750} = 47.8^\circ$, $d_{75} 0.647$, n for the yellow He line (5876) 1.00102.

O. B. HELFRICH

Questions of organic chemistry. I. Velocity of ring scission in gases. Trimethylene isomerization. M. TRAUTZ AND K. WINKLER. *J. prakt. Chem.* 104, 53-79(1922).—The trimethylene (A) isomerization to propylene (B) at 600° and the greater stability of B were shown. The $\text{A} \rightarrow \text{B}$ isomerization was found to be a reaction of the first order. Study of the effect of the wall on the gas reaction showed that this effect could be strongly repressed by choice of material and by rise in temp. The "heat of activation" was calcd. from expts. at $550\text{-}650^\circ$ to be 63,900 cal. The chem. "collision const." (*Stosskonstante*) on this basis was 1.00×10^{14} , showing the validity of reaction velocity isochore here. The % decompn. of A and B into CH_4 , C, and H_2 at the higher temps. was detd. by analysis.

O. B. HELFRICH

Distillation gases yielded by Trent amalgams, and ethylene found therein as a source of alcohol. J. D. DAVIS. *Bur. Mines Repts. Investigations* No. 2413, 8 pp.(1922).—Bury and Olander (*C. A.* 14, 826) have recently developed a method for converting C_2H_4 into EtOH , and de Loisy (*C. A.* 14, 1115) has perfected the method. Trent amalgams (Perrott and Kinney, *C. A.* 15, 3192) offer a promising source of C_2H_4 , as

they yield on distn. gases which are intermediate in C_2H_4 content between oil and coal. Expts. showed that at a distn. temp. of 800° one ton of amalgam yielded C_2H_4 equiv. to 32 gals. of EtOH, assuming a 100% conversion.

T. S. CARSWELL

Ethylene from Trent amalgams as a source of alcohol. J. D. DAVIS. *Chem. Met. Eng.* 27, 1087-8(1922).—See preceding abstr.

T. S. CARSWELL

The alkylglycerols. Preparation of the vinylalkylcarbinols. RAYMOND DELABY. *Compt. rend.* 175, 967-70(1922).—By the action of 1 mol. of the Grignard reagent on 1 mol. of acrolein the vinylalkylcarbinols are formed. By the addn. of Br_2 , conversion of the resulting bromohydrin to the diacetin, and hydrolysis of the latter with H_2O or MeOH, the corresponding alkylglycerol is formed in 60% yield. The vinylalkylcarbinols are obtained in 29-50% yield, after removing the higher boiling polymeric alcs. by distn. *in vacuo*, and distg. the well dried lower fraction at 760 mm. They form cryst. allophanates by the method of Béhal (cf. *C. A.* 13, 1839). *Vinylmethylcarbinol* b. $94-6^\circ$, d_4^{20} 0.854, d_4^{25} 0.835, n_D^{25} 1.487, mol. refraction 21.38; *allophanate*, m. $151-2^\circ$. *Vinylethylcarbinol*, b. $114-6^\circ$, b_{10} 37° , d_4^{20} 0.856, d_4^{25} 0.839, n_D^{25} 1.4182, M. R. 25.96; *allophanate*, m. $152-3^\circ$. *Vinylpropylcarbinol*, b. $133.5-4^\circ$, d_4^{20} 0.851, d_4^{25} 0.834, n_D^{25} 1.4215, M. R. 30.52; *allophanate*, m. $139.5-40^\circ$. *Vinylbutylcarbinol* (A), b. $153.5-4^\circ$, d_4^{20} 0.852, d_4^{25} 0.835, n_D^{25} 1.4275, M. R. 35.13; *allophanate*, m. $156.5-7^\circ$. Only traces of *vinylnonylcarbinol* could be isolated by this method (identified as the dibromide), nonane, nonene and octadecane being formed. A was resolved into its optical isomers (method of Pickard and Kenyon), $\alpha_D -23.3^\circ$.

I. P. ROLF

Preparation of methyl bromide. ARTUR BYGDÉN. *J. prakt. Chem.* 104, 285-8 (1922); cf. Steinkopf and Frommel, *Ber.* 38, 1865(1905); Bygdén, *C. A.* 5, 2817; Holt, *C. A.* 10, 1028; Steinkopf and Schwen, *C. A.* 16, 1390.—In the prepn. of MeBr (A) 95% H_2SO_4 is first dild. with H_2O , the MeOH is slowly added with cooling and then pulverized KBr is added; the flask with efflux condenser is slightly warmed; the evolved gases are passed through H_2O or NaOH to remove HBr and then through two bottles of concd. H_2SO_4 ; A is condensed in an ice-salt bath. The following quantities were used: (a) 520.5 g. 95% H_2SO_4 (3 mols.), 173.5 g. H_2O , 161.5 g. MeOH (3 mols.) and 200 g. KBr (1 mol.); after 1.75 hrs. 149.2 g. A or a 93.5% yield of A based on KBr; (b) H_2SO_4 , H_2O , KBr and time as in a and 108 g. MeOH (2 mols.) gave 155.3 g. A or a 97.3% yield; (c) as in a, using 67.3 g. MeOH (1.25 mols.), gave 153 g. A or a 95.9% yield. N. A. JANGE

Permanence of the Grignard reagent. HENRY GILMAN AND CHARLES H. MEYERS. *Ind. Eng. Chem.* 15, 61(1923); cf. *C. A.* 16, 1209.—Grignard reagents, of varying concns. in Et_2O , when protected from the atm., have been shown to undergo no change over a 6 months period.

H. GILMAN

The hydrogenation of aldehydes and ketones in the presence of pure and impure platinum black. M. FAULLEBIN. *Compt. rend.* 175, 1077-9(1922).—F. has found the presence of small amts. of $FeCl_3$ in Pt black catalyst gives better results in the hydrogenation of aldehydes and ketones than pure Pt black. Ir chloride instead of $FeCl_3$ has the same effect but does not give as good yields.

R. CHESTER ROBERTS

The mechanism of reaction of fatty diazo hydrocarbons. E. OLIVERI-MANDALÀ. *Gazz. chim. ital.* 52, 11, 103-12(1922).—This paper is a review of the reactions of these compds. and the conclusions follow. The diazo hydrocarbons are capable of giving rise to intramol. changes because of processes of addn. and of elimination; they can take place with unsatd. bonds [cf. e. g., the results obtained by O.-M. with bistetrazole (*C. A.* 14, 3412) and triazohydroquinol (*C. A.* 10, 1514)]. Secure conclusions as to the structure of diazo hydrocarbons themselves cannot be drawn from the structure of the alkyl derivs. obtained in esterification with the fatty diazo hydrocarbons. E. J. W.

Synthesis of substances of the disaccharide type from monohydroxy aldehydes. BURCKHARDT HELFERICH AND RUDOLF WEIDENHAGEN. *Ber.* 55B, 3348-54(1922).—

Because of the numerous OH groups in disaccharides, it was simpler to study compds. of this type with but two such groups. $\text{MeCH(OH)(CH}_2)_2\text{CHO}$ (A) refluxed 18 hrs. with CuSO_4 in dry Et_2O (all these condensations require careful exclusion of moisture) gave 53% of crude "*di-γ-hydroxyvaleraldehyde*" (B), $(\text{O}.\text{CHMe}.\text{CH}_2.\text{CH}_2.\text{CH}_2)_2\text{O}$, b_{11}

85–94°, which, shaken with concd. NaOH to remove A, extd. with Et_2O , and again distd., gave purer B, b_{11} 86–92°, mol. wt. in CHBr_3 , 183–5 (calcd. 186), d_{18} 1.0107, $[\text{M}]_D^{18}$ 48.62 (calcd. 48.91), mobile liquid, sol. 1:55 in H_2O , does not reduce Fehling soln. A 0.05% soln. of B in 5 N HCl was hydrolyzed, after 5 hrs. at room temp., to give 80% A, further identified as the *p*- $\text{BrC}_6\text{H}_4\text{N}_3\text{H}_2$ deriv. Similarly, $\text{EtCMe(OH)(CH}_2)_2\text{CHO}$ gave a "*dialdehyde*," b_{11} 121–5°, mol. wt. in $\text{C}_2\text{H}_4\text{Br}_2$, 205.5, 234.7 (calcd. 242.2), d_{18} 0.9678, $[\text{M}]_D^{18}$ 66.57 (calcd. 67.38), behaved on hydrolysis like B. $\text{MeCH(OH)(CH}_2)_3\text{CHO}$ gave, as above, a "*dialdehyde*," b_{12} 100–5°, mol. wt. in $\text{C}_2\text{H}_4\text{Br}_2$, 195.6 (calcd. 214.2), d_{18} 1.000, $[\text{M}]_D^{18}$ 57.35 (calcd. 58.14); a 1.7% soln. in 2 N HCl was 65% hydrolyzed after 14 hrs. at room temp.

BEN H. NICOLLET

Influence of pressure on the polymerization of *l*-glucosan. AMÉ PICIET AND J. H. ROSS. *Helvetica Chim. Acta* 5, 876–83(1922).—See C. A. 16, 2313. E. J. C.

Keto-enol equilibria and the Claisen rule. W. DIECKMANN. *Ber.* 55B, 2470–91 (1922).—According to Claisen's rule, in keto-enol isomers of analogous constitution the % of enol form at equil. increases with increase in acidity of the acyl groups. An apparent exception was the fact that, according to Meyer (*C. A.* 7, 993), the CO_2Me has a smaller enolizing power than the CO_2Et group, although there is no difference in their acidity, which, if it existed, should appear in the dissociation consts. of the Me and Et ester acids. A new study of this point has shown that the enol consts. (Meyer, *C. A.* 8, 1774) of the Me and Et esters of $\text{AcCH}_2\text{CO}_2\text{H}$ and also of $\text{BzCH}_2\text{CO}_2\text{H}$ are equal to each other and that, therefore, the CO_2Me and CO_2Et groups have the same enolizing power. Although the enol contents of the free esters at equil. differ materially ($\text{AcCH}_2\text{CO}_2\text{Et}$ 7.4, $\text{AcCH}_2\text{CO}_2\text{Me}$ 5, $\text{BzCH}_2\text{CO}_2\text{Et}$ 21.4, $\text{BzCH}_2\text{CO}_2\text{Me}$ 18.5% enol), this is due to the fact that the equil. esters are to be considered as solns. of the enol in the keto ester and that the keto Et ester favors the enol form to a higher degree, *i. e.*, has a higher desmotropic const., than the keto Me ester. In harmony with this view is the fact that the desmotropic consts. of AcOEt (0.164) and AcOMe (0.111) bear to each other the same relation (about 1.5:1) as do the equil. consts. of $\text{AcCH}_2\text{CO}_2\text{Et}$ and $\text{AcCH}_2\text{CO}_2\text{Me}$; the same is true of BzOEt and BzOMe , where the ratio of the desmotropic consts. (0.1835:0.15) to each other is 1.2:1, and $\text{BzCH}_2\text{CO}_2\text{Et}$ and $\text{BzCH}_2\text{CO}_2\text{Me}$. Although these apparent discrepancies thus fall in line with the Claisen rule, there occur in other cases material deviations which show that constitutional influence of another kind may be of decisive significance for the enolizing tendency. Thus, while the series AcCH_2Ac (33), AcCH_2Bz (120), BzCH_2Bz (350) (the values in parentheses being the enol consts.), formed by progressive replacement of Ac by Bz groups, obeys the rule, the % of enol at equil. in alc. and the enol consts., resp., of the Me derivs. of the above 3 compds. are as follows: AcCHMeAc 34, about 3.9; AcCHMeBz 7, 0.6; BzCHMeBz 0.3, about 0.02; here the replacement of Ac by Bz groups produces a large decrease in the enol const. Similarly, the enol const. of CHBz_3 is only about 10 as compared with about 78 for that of CHAcBz_2 . Again, while the β -ketonecarboxylic esters of the cyclopentane series are considerably more strongly acid (as shown, *e. g.*, by the lesser hydrolysis of their salts in H_2O) than those of the cyclohexane series and it had therefore been concluded that the former have the higher enol content (*Ann.* 317, 33(1901)), it has now been shown by the Br titration method that this conclusion is incorrect; the enol content at-equil. and the enol const. of Et β -cyclopentanonecarboxylate (A) are 4.5% and about 0.5 (only slightly higher than the values, about 3% and 0.23, for $\text{AcCH}_2\text{CO}_2\text{Et}$), and for

Et β -cyclohexanecarboxylate (B) 76% and about 12, resp. The great difference in the enol const. of these 2 compds. cannot be attributed to the difference in acidity of the acyl groups; it is probably dependent on the strain relationships in the rings, those in the 6-membered ring apparently favoring the enol formation, which involves the production of a C:C union, although this does not explain the higher acidity of the cyclopentane deriv. To obtain more light on this point, a no. of other β -ketonecarboxylic esters were studied. Et β -cycloheptanecarboxylate (C) has an enol const. of about 1.2 and an acidity similar to that of B, Et camphocarboxylate a const. of 0.04 and a very slight acidity. Di-Et cyclopentane-2,3-dione-1,4-dicarboxylate (D) and *ethyl cyclopentane-2,3-dione-1-carboxylate* (E) and their 5-Ph derivs. are stable in the enol form, both in the solid state and in soln. This great increase in the tendency to enolize, as compared with A, is explainable, in harmony with the Claisen rule, as due to the powerful influence of α -C:O groups in increasing the acidity, as shown by the high dissociation const. of α -ketonecarboxylic acids; possibly the change in strain relationships produced by substituting O for H₂ may also play a part. *Ethyl α -hydrindone- β -carboxylate* (F) has an enol const. of about 2.4 and is a relatively weak acid which cannot be titrated with alkali in aq. alc. while *ethyl β -hydrindone- α -carboxylate* (G) has a very high enol const. (even in alc. at equil. it is almost completely enolized) and such a high acidity that it can be quant. titrated as a monobasic acid in aq. alc. with alkali. The acyclic analogs of these esters show a much smaller acidity and materially smaller enol const.; BzCH(CH₂Ph)CO₂Et (H), the analog of F, has a materially smaller enol const. (about 0.3) than PhCH₂COCHPhCO₂Et (I), the analog of G, whose const. is 3.6. On the whole, then, the Claisen rule holds good only to a limited extent, and the enolizing tendency and acidity depend, in a not yet clearly defined, manifold manner, on other constitutional influences. This work has also shown again that the Meyer Br titration method can be very generally used and that his equation $K = EL$ (K = equil. const. = concn. enol./concn. ketone, E = enol const., L = the enolizing effect or "desmotropic const." of the solvent) holds quite well in most cases. In the Br titration of the unsubstituted 1,3-diketones, RCOCH₂COR', both the direct and the indirect methods yield the same results. With the monoalkyl derivs. the indirect method cannot be used in some cases, as the bromination products do not react smoothly and quant. with I₂, and the direct method has the disadvantage that with small amts. of substance and in very dil. soln. it is difficult to det. the end-point (permanent faint yellow color produced by free Br); in such cases satisfactory results have been obtained by adding a known amt. of alc. Br in excess to the well cooled alc. soln. and detg. the excess by adding KI and titrating the I which is immediately liberated in the cold. AcCH₂CO₂Et and AcCH₂CO₂Me at equil. at 20° in about 1% soln. show, in the same solvent, the same % of enol (EtOH 11.0, MeOH 6, C₆H₆ 18, AcOEt 14.1, AcOMe 10, BzOEt 15.5, BzOMe 13.1). The same is true of BzCH₂CO₂Et and BzCH₂CO₂Me (EtOH 24, MeOH 14.5, C₆H₆ 34, AcOEt 29.5, AcOMe 21.9, BzOEt 32.2, BzOMe 28). Enol content at equil. at 20° of AcCH₂MeAc without solvent 31.2, in 1% soln. in EtOH 33.8, in MeOH 20%; of BzCHMeAc (completely to remove the BzCH₂Ac from this compd. which, when pure, b₂₀ 152°, it is not enough to shake the methylation product with an amt. of alkali "equiv." to the excess of BzCH₂Ac used; it must be shaken with further small amts. of cold alkali until it gives a pure blue-violet FeCl₃ reaction in Et₂O) without solvent 5.7, in EtOH 7, in MeOH 3.7, in hexane 19.2; of BzCHMeBz (long needles from alc., m. 82-3°, gives no color with alc. FeCl₃ and no ppt. with alc. Cu(OAc)₂, prepd. by refluxing CH₂Bz₂ and the calcd. amt. of NaOEt in abs. alc. with an excess of MeI until the reaction is neutral) without solvent 0, in MeOH 0.15, in EtOH 0.3, in hexane about 1.6%. The enol form of the last compd., prepd. from the yellow soln. in the calcd. amt. of cold alc. NaOEt slowly poured into an excess of cold dil. mineral acid, seps. from alc. in

leaflets, m. 110°, gives an intense blue-violet FeCl_3 reaction in alc., is almost quant. extd. from Et_2O by the calcd. amt. of dil. KOH and almost completely pptd. by shaking with dil. $\text{Cu}(\text{OAc})_2$ as a light green *copper salt*, m. 245°; solubilities (in g.) of the enol and keto forms, resp., in 10 g. solvent at 20°: MeOH 0.12, 0.840; EtOH 0.155, 0.51; hexane 0.11, 0.062; the abs. equil. const. (0.01) calcd. from these soly. data by the van't Hoff-Dimroth law agrees with sufficient accuracy with that (0.023) calcd. from the enol content of the alc. soln. at equil. Enol content at equil. at 60° of CHBz_3 in MeOH 29, in EtOH 45, in C_6H_6 71; soly. at 20° in 100 parts solvent: EtOH 0.014, C_6H_6 0.2. Enol content of **A** (b_{11} 103°) at equil. without solvent 4.5, in MeOH 3.4, EtOH 6.4, C_6H_6 9.2, hexane 31%; enol form, crystals quite rapidly liquefying and changing into the equil. mixt. Enol content of **B** (b_{11} 106°) without solvent 76, in HCO_2H 13.2, MeOH 42.5, AcOH 42.75, EtOH 69, C_6H_6 72.51%; enol form, oil. **C**, b_{12} 110–5°, is obtained in 1 g. yield from 10 g. Et substrate heated about 4 hrs. under a reflux with 2 atoms Na powder at 120–40°, and is purified through the *copper salt*, light green crystals from C_6H_7 -benzine, m. 195°; it contains at equil. about 18% enol without solvent and 14% in EtOH, gives with 5 N NaOH a cryst. *sodium salt* and with PhNHNH_2 on the H_2O bath *1-phenyl-3,4-cycloheptano-5-pyrazolone*, m. 210° (the corresponding deriv. of **B**, m. 180°, not 165° as formerly given). **E**, from **D** boiled with aq. AcOH or HCO_2H , m. 52°, gives an intense brown-red FeCl_3 reaction in alc., yields a green Cu salt; *bis-phenylhydrazone*, yellow crystals from alc., m. 138°. *5-Phenyl derivative of E*, m. 102°, titrates sharply as a monobasic acid in aq. alc. with alkali and phenolphthalein; *bis-phenylhydrazone*, yellow crystals from alc., m. 181°; *2,3-methylquinoxalino derivative*, yellow crystals, m. 123°. **F**, from *o*- $\text{EtO}_2\text{CC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ heated several hrs. with Na in xylene, b_{20} 185°, contains at equil. without solvent about 25, in MeOH 14, in EtOH 23.3% enol; *copper salt*, m. 195–9°. **G**, from *o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{CO}_2\text{Et})_2$ boiled with 2 atoms of Na powder in C_6H_6 or with 1 mol. NaOH in alc., m. 68–9°, gives an intense corn flower-blue FeCl_3 test in alc.; *copper salt*, gray-brown, m. about 222°. The keto form of **I**, m. 80–1°; the enol form, readily obtained through the Na salt, seps. from alc. in leaflets m. 53°, gives an intense blue-violet FeCl_3 reaction in alc., is extd. only in traces from Et_2O by dil. alkali, is stable for months in pure state, gradually passes into the equil. mixt. (18.8% enol) at 100°; % of enol at equil. in MeOH 19, EtOH 31, C_6H_6 44.5. **H**, b_{14} 220°, contains about 4% enol without solvent and 4.1% in alc. C. A. R.

Esterification of creatine. A. W. DOX AND LESTER YODER. *J. Biol. Chem.* **54**, 671–3(1922).—Creatine was esterified, at room temp., by treating with the alc. and HCl. *Creatine methyl ester hydrochloride*, m. 139–40°. *Creatine ethyl ester hydrochloride*, m. 183°. *Creatine butyl ester hydrochloride*, m. 138°, decomps. 150°. All three ester hydrochlorides are sol. in H_2O and EtOH, insol. in Et_2O and yield difficultly sol. picrates. On heating above the m. p., all yield *creatinine hydrochloride*. No esterification occurred when iso-PrOH was used. I. GREENWALD

Glutaconic acid. II. P. E. VERKADE. *Rec. trav. chim.* **41**, 208–24(1922); cf. C. A. **15**, 366.—In a series of papers Thorpe, *et al.* (C. A. **6**, 1150, 1151, 3408, 3409; **7**, 336, 337, 1710; **8**, 69, 325; Curtis and Kenner, C. A. **8**, 1747) showed that in many alkyl and aryl substituted glutaconic acids, $\text{HO}_2\text{CCH}_2\text{CH}(\text{R})\text{CHCO}_2\text{H}$, the α - and γ -positions are identical owing to a "fluctuating" double bond. In the α,α -dialkyl derivs. this double bond is fixed and only the *cis-trans* isomerism occurs. When a so-called normal acid belonging to this "mobile" class is dehydrated under detd. conditions a hydroxyanhydride, a deriv. of 6-hydroxy- α -pyrone, is formed and on hydrating this compd. the original acid is generally formed by way of an intermediate unstable acid, which has a true double bond and should exist as *cis-trans* isomers. In the case of α - μ -ethyl- β -phenylglutaconic acid the 3 forms are known (Thorpe, Wood, C. A. **8**, 69). All the other unstable acids are known in but 1 form (probably the *cis*) except

in 1 case. V. has studied the behavior of glutaconic acid (A) itself on the basis of this theory. A has been obtained by many different methods but a detn. of the identity of these products has never been made. If the preps. are all identical it would show that one form of A has an abnormal stability and that it is formed under all conditions. A was prepd. (a) according to Conrad and Guthzeit (*Ann.* 222, 253(1883); see also *Ber.* 22, 1425(1889); *J. prakt. Chem.* [2] 73, 49(1906)) from malonic ester; (b) according to Pechmann (*Ann.* 261, 157(1891); *Ber.* 24, 3250(1891)) and Blaise (*Bull. soc. chim.* [3] 29, 1013(1903)) from citric acid; (c) according to Fichter and Dreyfus (*Ber.* 33, 1452(1900)) from β -hydroxyglutaric acid; (d) or by boiling the latter compd. with H_2SO_4 (v. Pechmann, Jenisch, *Ber.* 24, 3250(1891)); (e) or from cumalic acid (v. Pechmann, *Ann.* 264, 301(1891)); (f) by condensing acrylic ester with N_2CHCO_2Et (Buchner, *Ber.* 23, 703(1890); *Ann.* 273, 238(1893)). In this latter method *cis*- and *trans*-cyclopropane-1,2-dicarboxylic acid as well as A are obtained. V. describes the sepn. of the 3 acids. A obtained by all these methods has nearly the same m. p. (136 $^{\circ}$), which remains unchanged on mixing the various preps. No differences could be detd. so that it is certain that all methods give the same acid. The identity of these preps. was further confirmed by detns. of the dissociation consts. at 0 $^{\circ}$, 25 $^{\circ}$ and 45 $^{\circ}$ (Bösescken, *C. A.* 11, 2895). Previous attempts to transform A into isomers are reviewed and 5 different fruitless attempts to do so by means of sunlight, which was effective in converting malic into fumaric acid (Ciamician, Silber, *Ber.* 36, 4267(1903)), are described. One form of A thus stands out sharply over its isomers in its stability. This exceptional behavior suggests that it ought not to be considered as one of a *cis-trans* pair of isomers. The formula $HO_2CCHCH_2CHCO_2H$ revived by Thorpe (*C. A.* 6, 3409) represents

some of the facts but V. prefers the Erlenmeyer type $HO_2C \cdot \overset{\text{H}}{\underset{\text{H}}{\text{CH}}} \cdot CH \cdot CO_2H$, since it

readily permits of the formation of α,β - and α,γ -dibromoglutaric acid (V. and Coos, *C. A.* 15, 366) for instance. The cond. of solns. of A at 25 $^{\circ}$ does not change in 5 hrs. so that an isomerization is not involved unless it occurs very rapidly. $K^{25} = 1.76 \times 10^{-4}$ for A prepd. in the various ways (cf. *Rec. trav. chim.* 35, 79(1915), for the data). For glutaric acid $K = 4.7 \times 10^{-6}$ so that transformation into A by putting in a "double bond" makes it a 3-times stronger acid. Other similar cases are reviewed. The formula of A proposed, if considered to be rigid, provides for the existence of 2 optically active isomers. V. considers the H to be in continual movement in which case this is not possible. V. detd. the dissoc. const. at 45 $^{\circ}$ ($K^{45} \approx 1.64 \times 10^{-4}$) in order to exclude a possible partial isomerization at high temps. It is concluded that K reaches a max. between 0 $^{\circ}$ and 45 $^{\circ}$.

E. J. WITZEMANN

Determination of the constitution of hydroxy- and aminochloro-propanes by kinetic methods. I. SMITH AND B. PLATON. *Ber.* 55B, 3143-55(1922).—The detn. of the constitution was carried out by measuring the velocity at which the chlorohydrin mixt. is decompd. by $Ba(OH)_2$ (*C. A.* 13, 1461). $MeCH(OH)CH_2Cl$ gave a bimol. velocity coeff. at $t = 0$ of $k_0 = 14.3$, while the corresponding value for $MeCHClCH_2OH$ was found to be about 4. The coeff. of a mixt. of the two isomers lies between these limits and shows a marked decrease with increasing degree of decompn. The chlorohydrin from $dL-MeCH(NH_2)CH_2Cl$, by diazotization, is almost pure α -form, while that prepd. from $MeCHClCH_2NH_2$ contains about 60% α -form. The rate of decompn. of the amine pierates by $Ba(OH)_2$ was also studied; the *dl*-amine gave a const. of 0.50, while the isomer gave a const. of 0.067. Since the reaction between chloroamines and alkali may occur at more points than that between the chlorohydrin and alkali, it is correctly assumed that that amine which is decompd. more rapidly has the Cl at the end of the chain.

C. J. WESR

Acetone compound of anhydro-enneaheptitol. Acetone compounds of multivalent alcohols. C. MANNICH AND W. BROSE. *Ber.* 55B, 3155-7(1922).—In repeating Tollen's expt. on the condensation of AcMe and HCHO (*Ber.* 27, 1089), in which the only variation was the use of a slight excess of H_2SO_4 in place of $(\text{CO}_2\text{H})_2$ for the removal of the dissolved CaCO_3 , it was observed that when AcMe was stirred with the sirup, the mass became warm and the *diaceton compound of anhydro-enneaheptitol*, $\text{C}_{18}\text{H}_{38}\text{O}_8$, sep'd. as leaflets, m. about 229° , and starting to sublime at 100° . Upon distn. with a small amt. of dil. HCl, it decomps. into AcMe and anhydro-enneaheptitol (A). If, on the other hand, a drop of concd. HCl is added to a suspension of A in AcMe, heat is evolved and the mass solidifies to a cryst. mass of the di-AcMe compd. Heating with AcMe gives the *diaceton monoacetate*, strongly refractive needles, m. 140° .

C. J. WEST

Progress toward the artificial synthesis of carbohydrates and proteins. R. W. THATCHER. *J. Ind. Eng. Chem.* 14, 1146-7(1922).—A resumé of recent developments.

T. S. CARSWELL

Diacetoneglucose. P. A. LEVENE AND G. M. MEYER. *J. Biol. Chem.* 54, 805-13 (1922).—On treating diacetoneglucose with Me_2SO_4 and NaOH, *3-methyldiaceton-glucose* was obtained in the form of a sirup. Upon hydrolysis with HCl, this yielded *3-methylglucose*, m. 158° , $[\alpha]_D^{20} 57^\circ$ in 1% soln. (cf. Irvine and Scott, *C. A.* 7, 1167). Upon oxidation with 50% HNO_3 , this was converted into *1,4-anhydro-3-methylsaccharic acid*, sinters 190° , m. $206-7^\circ$; $[\alpha]_D^{20} 15^\circ$ in 0.5% soln. The AcMe groups in diacetoneglucose are therefore not on C atoms 1,2 and 3,5 but probably on 1,2 and 5,6. I. GREENWALD

Reduction of benzylidene-1-ethyl-2-diazogluconate. P. A. LEVENE. *J. Biol. Chem.* 54, 809-13(1922); cf. *C. A.* 16, 3877.—*Ethyl 2-diazo-5,6-benzalgluconate* (benzylidene-1-ethyl-2-diazogluconate), dissolved in iso-PrOH, was reduced by Al-Hg to a mixt. of *ethyl 2-desoxy-5,6-benzalgluconate* or *mannonate* (benzylidene-1-ethyl-2-desoxygluconate or *mannonate*) m. 124° , $[\alpha]_D^{20} -28.0^\circ$ in 1% soln., insol. in H_2O and acids, sol. in Et_2O , EtOH, MeOH, AcMe and *ethyl benzalchitosaminatate* (benzylidene-ethyl-chitosaminatate), $[\alpha]_D^{20} -15.0^\circ$ in 1% soln., consequently free from its epimer. An attempt to reduce *1-amino-2,3-anhydro-5,6-benzalgluconic* or *mannonic acid* (benzylidene-1-amino-2,3-anhydrogluconate or *mannonate*) in the same manner was unsuccessful, the substance being recovered unchanged. I. GREENWALD

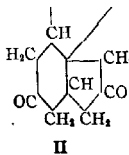
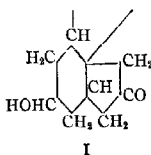
Mutarotation. I. C. N. RIBBER. *Ber.* 55B, 3132-43(1922).—In spite of the fact that the phenomenon of mutarotation has been known for 76 yrs., there is no certainty as to its cause. Attempts to link this with changes in other phys. properties, such as density and refractive index, have not been altogether successful. R. found a very slight increase (of the order of 0.00015) in the refractive index but feels that these values are not sufficiently accurate for the purpose. By using a special dilatometer (detecting a change in vol. of 0.0000001) it is shown that there is an increase in vol. of the soln. during mutarotation and that this follows the laws of an unimol. reaction, which is known to be true of the decrease of the rotation. Using a soln. of d. 1.03619, the vol. is shown to increase from 1.0000000 to 1.0001446. In connection with these results it is necessary to det. whether every substance which shows mutarotation shows the same change in vol. in soln., and the opposite and whether optically inactive substances behave similarly. Preliminary expts. indicate that lactose solns. show a dilatation, maltose solns. suffer a contraction in vol., galactose shows at 1st a dilatation and then a contraction, sucrose does not change in vol., nor do mannitol and dulcitol. AcH shows a noticeable dilatation in 30% aq. soln., while AcMe undergoes a strong and rapid contraction. EtOH shows a small dilatation. $\text{CO}(\text{NH}_2)_2$ solns. show no vol. change. The possibility of applying this method of expt. to other investigations is briefly outlined.

C. J. WEST

Pentosans. IV. Hydrolysis of xylans with diluted acids. ÉMIL HEUSER AND LUDWIG BRUNNER. *J. prakt. Chem.* **104**, 264–81 (1922); cf. *C. A.* **16**, 1082; Tollens and Hauers *Ber.* **38**, 3306 (1903).—When the xylans (A) from bleached straw cellulose are hydrolyzed with dil. acids in the prepn. of xylose (B) the yields are low because of the formation of some furfural (C) and a study has been made to det. the quant. mechanism of this reaction. Weighed quantities of A with 8 parts of dil. acid of known concn. were heated in a water bath at 95°; C formed in the reaction was collected in a condenser connected to a measuring flask containing phloroglucinol-HCl; since C is volatile only with steam very little was obtained by this collection; the greater part of C remained in the reaction mixt. After definite periods of time the soln. of hydrolytic products was neutralized with Na₂CO₃ and then dild. to a definite vol. in a graduated flask; the sugar value was detd. by Bertrand's method (cf. *Bull. soc. chim.* **35**, 1285 (1906)); control detns. of the sugar value were made by conversion to C and detd. by the Tollens and Koeber method; total C from sugar and that evolved during the reaction were detd. on a portion of the soln.; these values are low because of partial polymerization of the evolved C during the course of the hydrolysis and depend upon time and the concn. of the hydrolyzing acid; the quantity of C formed during hydrolysis only was detd. on a duplicate reaction by omitting the hydrolyzing acid. Hydrolysis of A with: (a) 12% HCl gave 88% B after 5 min.; the max. B is formed between 5–10 min.; after 10 min. the amt. of B decreased because of conversion to C; (b) 5% HCl gave a max. of 90% B after 0.5 hr.; (c) 12% H₂SO₄ gave a max. of 85% B after 1 hr. Continued action of the acids above leads to formation of C and then polymerization and decompn. of C. B was prepd. in 67% yield by boiling under a reflux for 70 min. 10 g. air-dried A with 400 cc. 5% H₂SO₄, neutralizing with BaCO₃, filtering and evapg. on a water bath; the BaSO₄ which seps. is removed by filtration from time to time; after 10 days the sirup crysts.; crystals from EtOH, m. 143.2°; B was identified by conversion to the osazone, crystals from H₂O and then from Me₂CO, m. 157.3°; the bromocadmium xylonate (cf. Bertrand, *Ber.* **35**, 1460 (1902)) was prepd. B was also prepd. in 50.6% yield by hydrolysis of A with 5% HCl for 0.5 hr. and neutralization of the HCl with PbCO₃.

N. A. LANGE

Constitution of the bile acids. IV. Reductodehydrocholic acid. W. BORSCHET AND F. HALLWASZ. *Ber.* **55B**, 3318–23 (1922).—Reductodehydrocholic acid (I) (cf. Hammarsten, *Ber.* **14**, 71 (1881), and Schenck, *C. A.* **4**, 1624; **5**, 1272) has been made in new ways, which throw light on its constitution. Dehydrocholic acid (II), reduced by H₂ with Pd black, gave 75% of the ethyl ester (A) of I, m. 153–4°. A was also obtained in 80% yield by reduction of II with Al-Hg and esterification; dioxime of A, m. 230–40°. Sapon. of A gave I, crystals with 1 H₂O, sinters above 112°, losing H₂O, and m. 186–7°. The methyl ester of I, m. 155–6°; its dioxime, m. 258° (slight decompn.). The Et ester of diketocholonic acid (B), m. 143°, was obtained by vacuum distn. of A; its dioxime, colorless needles from alc., m. 228°. Diketocholonic acid itself was formed as prisms, m. 174°, by sapon. of B. With Pd black and H₂, B gave the ethyl ester of β -diketocholonic acid, m. 152–3°; dioxime, m. 242° (decompn.). α -Diketocholonic acid (C), reduced with Na-Hg in CO₂, gave hydroxyketocholonic acid, m. 160°; Et ester, m. 131–2°. The mono-*q*-cyano-*z*-nitrophenylhydrazone of C, m. 270° (decompn.).



V. Transition from the cholic acid series to the lithocholic acid series. *Ibid* 3324-31.—Dehydrocholic acid (II, above), digested 1 day with $\text{NH}_2\text{NHCONH}_2$, gave a *triseMICARBAZONE* (D), amorphous, turns brown at 290° and decomp. soon afterwards. Heated 8 hrs. at 200° with NaOEt in alc., D gave cholanolic acid (E), m. 161° ; Et ester m. 91° . I (above) gave similarly a *disemicarbazone* (F), not quite pure, gelatinous, darkens about 300° . Heated at 180° for 8 hrs. with NaOEt in alc., F gave 20% of lithocholic acid (G) (cf. Wieland and Weyland, *C. A.* 15, 1730) as white leaflets, m. $185-6^\circ$, $[\alpha]_D^{19}$ 32.72° in 1.53% abs. alc. soln. With CH_3N_3 , G gave a *methyl ester*, long needles, m. 130° . Dehydrolithocholic acid (H) gave similarly a *methyl ester*, leaflets, m. 117° , whose *oxime*, needles, m. 148° . As above, bilianic acid formed a *disemicarbazone*, darkening above 280° , and giving when hydrolyzed with NaOEt , 8-10% of lithobilianic acid (J), m. 279° as described by W. and W. Desoxybilianic acid, through its *semicarbazone* (decomps. $215-20^\circ$) also gave J in 20% yield. The *trimethyl ester* of J, needles, m. 112° . Isobilianic acid (K) formed a resinous *disemicarbazone*, decomp. above 280° , which was hydrolyzed to *isolithobilianic acid* (L) (m. 261°), purified through the *trimethyl ester*, m. $103-4^\circ$. L was also prepd. from K by the Clemmensen reduction with amalgamated Zn, but the method was capricious. BEN H. NICOLET

Unsaturated bile acids. III. Relations of apocholic acid, dihydroxycholeonic acid (m. 260°) and cholic acid to desoxycholic acid. F. BOEDECKER AND H. VOLK. *Ber.* 55B, 2302-9(1922); cf. *C. A.* 16, 1217.—It had been found that cholic acid (A) with dehydrating agents yields chiefly 2 unsatd. acids, $\text{C}_{24}\text{H}_{46}\text{O}_4$, apocholic (B) and dihydroxycholeonic (C), m. 260° . B, like desoxycholic acid (D), forms with many org. substances addn. products analogous to the choleic acids (E). It was concluded that B is closely related to D and that probably the two HO groups occupy the same positions in both acids, although no direct proof of this, by hydrogenation of B, could be obtained. Further study of B has now shown that on degradation with Br it gives about 40% of a *dihydroxycholadienic acid* (F), which can no longer form E-like addn. products and takes up 1 mol. H_2 to form an acid identical in all respects except optical activity with B, whence the non-hydrogenizable double bond of F must be identical with the double bond in B. Since C forms no E-like addn. products and it differs considerably in chem. and phys. properties from B it had been concluded that in its formation another HO group than that in the formation of B is involved in the dehydration, but this assumption has been found to be incorrect. If C is degraded with Br like B it gives F in even better yield (at least 60%), whence there can be no doubt that B and C are formed by elimination of the same HO group from A and that they differ only in the positions of the unsatd. unions. C easily takes up 1 mol. H_2 and yields D quant. Both HO groups in B and C therefore occupy the same positions as those in D; at the same time this is the first direct proof that two HO groups of A are identical with those of D and hence that A passes into D by elimination of 1 mol. of H_2O and addn. of one of H_2 . Seeing that the hydrogenation product of C is identical, even optically, with natural D, it is probable that in the formation of C from A no asym. C atom of the D is involved, and that the double bond of C lies between 2 sec. C atoms. F, obtained in 14-6 g. yield from 30 g. AcOH -B in 250 cc. MeOH at -10° slowly treated with 3.6 cc. Br in 50 cc. MeOH , poured into ice water, which ppts. a soft yellow tar, kneaded until it falls to a powder, filtered, washed, dried and sapond. with alc. KOH, m. $245-7^\circ$, decolorizes alk. KMnO_4 and Br in MeOH , $[\alpha]_D^{19}$ 23.0° (abs. alc.). The alkali salts are sol. in H_2O and alc.; the Mg and Ba salts are pptd. from not too dil. solns. of the alkali salts as oils, which become cryst. on boiling; *silver salt*, fine needles; *methyl ester*, from the acid with CH_3N_3 , sinters 79° , m. 85° . C. A. R.

Betulin. HEINRICH SCHULZE AND KURT PIEROH. *Ber.* 55B, 2332-46(1922).—Betulin (A) seps. from alc. on rapid cooling in fine asbestos-like needles with 0.5 mol.,

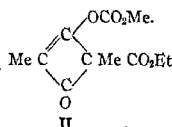
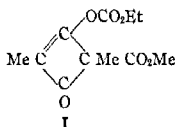
on slow cooling in stout rhombic needles with 1 mol. EtOH, m. 251-2°; the last 0.5 mol. of EtOH can be driven off only at 120-5° and this doubtless explains the varying results which different investigators have obtained for the compn. of **A**. S. and P. find that it has the compn. $C_{28}H_{48}O_2$ or $C_{28}H_{46}O_2$, $[\alpha]_D^{15}$ 19.96° (C_6H_5N). With boiling Ac_2O it yields a *diacetyl derivative*, stout rhombic prisms, m. 216-7°, $[\alpha]_D^{15}$ 21.99° ($CHCl_3$). *Acid phthalate*, from **A** dissolved in fused $C_6H_5(CO)_2O$, fine felted needles with $2H_2O$ or $1EtOH$ from dil. alc., m. 180-2° (gas evolution), $[\alpha]_D^{15}$ 24.48° ($CHCl_3$); *silver salt* of the ester. When **A** was refluxed 45 min. with 8 parts of 90-5% HCO_2H , there was obtained, instead of the expected diformate of **A**, 85% of a *monoformate*, stout rhombic needles from C_6H_6 , m. 311-2°, $[\alpha]_D^{15}$ 51.08° ($CHCl_3$), of an isomer, *allobetulin* (**B**), of **A** (obtained from the formate by refluxing with KOH in alc. and C_6H_6), triangular mono- or triclinal tablets from alc., m. 260-1°, $[\alpha]_D^{15}$ 48.25° ($CHCl_3$); *acetate*, 6-sided rhombic tablets from $EtOH-C_6H_6$, $[\alpha]_D^{15}$ 54.16° ($CHCl_3$); *benzoate*, from **B** heated 1 hr. at 170° with 2 parts Bz_2O , apparently monoclinic tablets from $EtOH-C_6H_6$, m. 275-6°, $[\alpha]_D^{15}$ 70.26° ($CHCl_3$); *acid phthalate*, fine felted needles from alc., m. 260-1° (faint gas evolution), $[\alpha]_D^{15}$ 58.20°; *silver salt* of the acid phthalate, leaflets, sol. in alc. NH_3 ; *acid succinate*, from **B** and fused succinic anhydride, fine leaflets from $EtOH-C_6H_6$, m. 265-6°, $[\alpha]_D^{15}$ 48.01° ($CHCl_3$), yields a *silver salt*, fine leaflets. This rearrangement of **A** into **B** is not due to a specific action of HCO_2H as it can also be brought about through the acetate by boiling **A** in glacial $AcOH$ contg. concd. HCl but the reaction is not so smooth as with HCO_2H , for the HCl partly resinifies the sensitive **A**. As compared with **A** and its derivs., **B** and its derivs. have higher optical rotations, higher m. ps., and smaller solubilities and are more resistant towards chem. agents. From their properties and reactions, **A** and **B** are best classed with the *d*-rotatory phytosterols. The most striking reaction which they have in common with the latter is the Liebermann cholesterol test, and also perhaps the Salkowski-Hesse test. Moreover, **A** in its behavior very closely resembles the diacid sterol onocol, $C_{28}H_{46}O_2$, obtained from the roots of *Oninos spinosa*, while **B** shows a very great similarity to the α - and β -amyrin on the one hand, and the lupeol, on the other, found in elerni resin. Thus, with CrO_3 in $AcOH$ at 60°, **B** gives a ketone, *allobetulone*, $C_{28}H_{46}O_2$ or $C_{28}H_{48}O_2$, rhombic needles from alc., m. 230-1°, $[\alpha]_D^{15}$ 84.40°; *oxime*, leaflets, m. 285-90° (decompu.); *phenylhydrazone*, faintly yellow leaflets, m. 223° (decompu.). Again, **B** treated in $CHCl_3$ with PCl_5 or P_2O_5 loses 1 mol. H_2O , yielding *apoallobetulin*, stout rhombic needles from alc., m. 198-200°, $[\alpha]_D^{15}$ 74.78° ($CHCl_3$), decolorizes Br in $CHCl_3$ with evolution of HBr . Finally, the acetate of **B** with CrO_3 in boiling $AcOH$ gives the *acetate*, leaflets from $AcOH$, does not m. 360°, sublimes without melting and almost without decompn. in fine hairs, $[\alpha]_D^{15}$ 54.34° ($CHCl_3$) of *oxyallobetulin*, $C_{28}H_{46}O_4$ or $C_{28}H_{48}O_4$, fine felted needles from alc., sublimes without melting.

C. A. R.

Melanin formation from organic substances. O. ADLER AND W. WIECHOWSKI. *Ber.* 55B, 3030-8(1922).—In testing a substance for melanin formation, 1-2 dg. were dissolved or suspended in 10-12 cc. H_2O and 3-4 drops $N FeCl_3$ added. The mixt. was divided into 2 parts, in order to examine the action of $FeCl_3$ alone, while to the other 0.2-0.5 cc. 3% H_2O_2 was added. On short heating the liquid turns dark or nearly black if the compd. is capable of forming melanin. Addition of $NaOH$ causes a characteristic deepening of the color. The reaction must be carried out in neutral or slightly alk. soln. 382 compds. were tested and are listed as giving a positive or negative reaction. No aliphatic compd. tested gave the reaction; this occurs only with cyclic compds. Certain classes of compds. give little or no reaction, such as the terpenes, the Ph_3CH -, the C_6H_5N -, the C_6H_5 - and the phenanthrene groups; on the other hand, $PhNH_2$ and homologs, $PhNHNH_2$ and homologs and substitution products, the phenols, quinones, aromatic monoaldehydes and ketones, mono- CO_2H acids and phenolmonocar-

boxylic acids give a strong positive reaction. The entrance of a halogen in the nucleus inhibits or prevents the reaction. Sulfonation has little or no effect. Aromatic As compds. are negative, even though the parent compds. are positive. An NH_2 group accelerates the reaction. The NO_2 group appears to have no influence but the presence of a Me group retards or prevents the formation of melanin. In the case of esters and ethers, one must consider the ease of decompn. and also the effect of oxidizing agents. Most of these compds. tested reacted positively. C. J. West

Relations between the dimeric ketenes and 1,3-cyclobutanedione and its derivatives. W. DIECKMANN AND ADOLF WITTMANN. *Ber.* 55B, 3331-47(1922).—The polymeric ketenes have been formulated by Staudinger as 1,3-cyclobutanedione derivs., while Schroeter (*C. A.* 11, 2776; 15, 865) maintains that they are mol. compds. D. and W. sustain the views of Staudinger. Me 2,4-dimethyl-1,3-cyclobutanedione-2-carboxylate (A) gave on evapn. in a desiccator with NaOMe a sodium salt, which with ClCO_2Et yielded 60% of methyl *O*-carbethoxy-2,4-dimethyl-1-cyclobuten-1-ol-3-one-4-carboxylate (I), b_{11} 173-5°, crystals from ligroin m. 66-8°. Hydrolysis of I with NaOHt (24 hrs.



at room temp.) gave A. Similarly, ethyl *O*-carbethoxy-2,4-dimethyl-1-cyclobuten-1-ol-3-one-4-carboxylate (II) was obtained as an oil, b_{11} 173-5°, which would not cryst., and gave on hydrolysis the Et ester corresponding to A, from which it had been obtained. Separate expts. showed that interchange of alkyl groups did not take place under these conditions. The fact that I and II are not identical, invalidates the chief evidence of Schroeter. $\text{MeCOCHMeCO}_2\text{Me}$ was converted, with Na powder and BzCl , both in Et_2O , to $\text{BzCOCHAcCO}_2\text{Me}$ (C), b_{10} 173-4°, crystals from MeOH, m. 79-80°. C was "catalytically" hydrolyzed in 0.5 hr., with 0.05 mol. NaOMe in MeOH, to $\text{BzCOCHMeCO}_2\text{Me}$ (D), b_{10} 141-2°, thoroughly identified. Under similar conditions, $\text{BzCHMeCO}_2\text{Me}$ gave with AcCl the *O*-ester, b_{10} 161°; hydrolysis as above gave D. $\text{AcCMe}(\text{CO}_2\text{Me})_2$ and $\text{AcCEt}(\text{CO}_2\text{Et})_2$ gave with 0.05 mol. NaOR good yields of $\text{MeCH}(\text{CO}_2\text{Me})_2$ and $\text{EtCH}(\text{CO}_2\text{Et})_2$, resp., showing that this "catalytic" hydrolysis is characteristic of the grouping $-\text{COCR}(\text{CO}_2\text{R})\text{CO}-$ (cf. Staudinger). It was also shown that $\text{AcCMe}_2\text{CO}_2\text{Me}$ and $\text{AcCEt}_2\text{CO}_2\text{Et}$ readily exchange their ester radicals in the presence of NaOMe and NaOEt, resp., differing thus from A and B. Further arguments which improve the case are presented. BEN H. NICOLET

Aromatic chloroamines. II. STEFFAN GOLDSCHMIDT AND LUDWIG STROHMENGER. *Ber.* 55B, 2450-70(1922); cf. *C. A.* 8, 105.—The study of the aromatic chloroamines has been continued in order to obtain more knowledge on this difficultly obtainable class of compds. and especially on their reactions in connection with the question of PhNH_2 oxidation (*C. A.* 14, 2200). The 3 isomeric $\text{O}_2\text{NC}_6\text{H}_4\text{NCl}_2$ can be obtained in cryst. form, as had been hoped, but as respects instability they are not far removed from PhNCl_2 . Like PhNCl_2 they are prepd. from the amine and HOCl in Et_2O at -20° to -30° and are isolated by concg. at -20° and pptg. with petr. ether. They can be kept unchanged for days at -70° ; at room temp. they soon become discolored and deflagrate. Their constitution and purity were detd. by treating with acidified KI and titrating the liberated I. *Pentachlorophenyl-N-dichloroamine* (*heptachloroaniline*) (A), however, is stable at room temp. for weeks if carefully protected from moisture but otherwise shows the characteristic properties of the chloroamines, deflagrates at higher temps. and decomp. in boiling PhMe into Cl and *decachloroazobenzene* (B). While

negative substituents (especially in the *o*- and *p*-positions) in the C_6H_5 nucleus thus increase the stability and power to cryst. of the chloroamines, positive groups decrease their stability; *m*- $MeC_6H_4NCl_2$ (C) and 2,3,5- $Me_3C_6H_2NCl_2$ (D) could be obtained only in soln. under the most exact conditions. The aromatic chloroamines are very sensitive towards acids; on standing in solns., which always contain some HCl as the result of side reactions, more quickly on adding HCl in Et_2O , they rearrange into nucleus-chlorinated compds. p - $O_2NC_6H_4NCl_2$ gives 2,6,4- $Cl_3(O_2N)C_6H_2NH_2$. The *o*-compd. yields various products, depending on the amt. of HOCl used in its prepn.; with about the calcd. amt. of HOCl and subsequent addn. of HCl in Et_2O is obtained 4,2- $Cl_2(O_2N)C_6H_2NH_2$, while with a 30% excess of HOCl the product is 4,6,2- $Cl_3(O_2N)C_6H_2NH_2$. This is certainly due to a partial hydrolysis by larger amts. of HCl, for if the Et_2O soln. of the chloroamine alone is allowed to stand, only the di-Cl compd. is formed. Entirely different from the decompn. in the presence of HCl is the autodecompn., which proceeds with liberation of free Cl. If the decompn. of p - $O_2NC_6H_4NCl_2$, which deflagrates at room temp., is carried out in a closed app. and the liberated gas is passed into KI, it is found that $\frac{1}{6}$ of the Cl combined with the N is set free, small amts. of HCl are formed (by chlorination processes) and from the residue only $(p$ - $O_2NC_6H_4N$) $_2$ can be isolated. The same process takes place slowly at low temps. (-70°) and may be explained by assuming that the radical $O_2NC_6H_4N\cdot$ is first formed. The course of the autodecompn. in solvents depends on the temp. In boiling Et_2O the Cl is split off slowly and chlorinates the Et_2O with formation of HCl which produces a rearrangement into the nucleus-chlorinated product. In higher boiling solvents, however, the liberation of the Cl is almost instantaneous, much more rapid than the rearrangement produced by the HCl resulting from the chlorination of the solvent. The rearrangement products are identical with those obtained by direct chlorination of the amines and all the above facts indicate that this latter reaction proceeds according to the scheme $PhNH_2 + Cl_2 \rightarrow PhNHCl + HCl \rightarrow ClC_6H_4NH_2 + HCl$ rather than through addn. at the double bond and subsequent elimination of HCl. The Cl in the aromatic chloroamines is extraordinarily reactive; it reacts with Cu powder, NaOEt, NH_3 , $Na_2S_2O_3$ and neutral KI, the end products being $PhN:NPh$ and $PhN:C_6H_4NH$ or their substitution products. C with KI yields *N-m-tolyltoluquinonediimide* (E) and $(ClMeC_6H_3N)_2$ and D gives *N-p-chlorocumylcumoquinonediimide*, $ClMe_2C_6H_3N:C_6H_4Me_2NH$ (F) and *di-chloroazocumene* (G). The formation of the chlorinated F can be explained only by secondary chlorination of the Cl-free substance, for a primary partial nucleus rearrangement would never lead to a mono-Cl deriv.; in fact, if the *p*-position were occupied, no quinoneimide at all would be formed. Unlike the chloroamines of $PhNH_2$, $MeC_6H_4NH_2$ and cumidine, those of the $O_2NC_6H_4NH_2$ yield the corresponding azo compds. exclusively and none of the quinonediimides even when the *p*-positions to the NH_2 group are unoccupied. Only *o*- $O_2NC_6H_4NCl_2$ offers an exception to the above general behavior; with KI it yields 4,4' (?) *diiodo-2,2'-dinitroazobenzene* (H), probably according to the scheme $2O_2NC_6H_4NCl_2 + 4KI \rightarrow 2O_2NC_6H_4NI_2 \rightarrow 2I(O_2N)C_6H_4N = + 2HI \rightarrow [I(O_2N)C_6H_4N]_2$, and $O_2NC_6H_4NI_2 + 2HI \rightarrow O_2NC_6H_4NH_2 + 2I$. The above facts confirm the view that the reactions and autodecomps. of the chloroamines proceed through an intermediate radical $RN\cdot$. *N-Dichloro-p-nitroaniline*, reddish yellowish prisms, m. about 50° . *4-Nitro-2,6-dichloroaniline*, light yellow felted needles from alc., m. $189-90^\circ$. *N-Dichloro-o-nitroaniline*, light yellow to brownish prisms, m. $48-50^\circ$ (complete decompn.); quickly heated to boiling in CCl_4 it gives $(o$ - $O_2NC_6H_3N$) $_2$, m. $209-10^\circ$ (given as $194-5^\circ$ in the literature [Ber. 33, 2715(1900)]). H, slender, intensely yellow prisms from AcOH contg. a trace of CrO_3 , m. $248-9^\circ$. *N-Dichloro-m-nitroaniline*. 1-Dichloroamino-2,3,5-trimethylbenzene (*N-dichloro- α -pseudo-cumidine*) (D) is obtained only in the yellow-red Et_2O soln. which, slowly added to aq.

alc. KI at -30° , kept 0.5 hr. at that temp., shaken several hrs. with a large excess of $\text{Na}_2\text{S}_2\text{O}_3$ in Na_2CO_3 , sepd. from the aq. layer, dried with K_2CO_3 , shaken with Zn dust and AcOH until the soln. is light yellow, filtered, shaken with dil. NH_4OH , then with H_2O , dried with K_2CO_3 and treated with anhyd. $(\text{CO}_2\text{H})_2$, yields a voluminous oxalate giving on decompn. with NH_4OH and extrn. with Et_2O *chloroaminodimethylamine* (I), felted needles from abs. alc., m. $167-8^\circ$; the alc. mother liquors on steam distn. yield *4(?)*-chloro-2,3,5-trimethylaniline (J), needles from petr. ether, m. $119.5-1.0^\circ$, and the Et_2O filtrate from the oxalate, freed from $(\text{CO}_2\text{H})_2$ by shaking with dil. NH_4OH , dried with Na_2SO_4 and shaken several hrs. with PbO_2 , yields *4,4'(?)-dichloro-2,3,5,2',3',5'-hexamethylazobenzene* (G), highly red needles from AcOH, m. $189-90^\circ$. F, from I in Et_2O -petr. ether shaken 3 hrs. with PbO_2 and a little Na_2SO_4 , thick dark red prisms with dull surface luster from petr. ether, m. $113-6^\circ$, forms deep red concd., red-yellowish dil. solns., gives with acids a blue-violet color paling out on standing, converted in alc. by 1-2 drops dil. H_2SO_4 into J and cumoquinone. *1-Dichloroamino-3-methylbenzene* (*N*-dichloro-*m*-toluidine) (C) is likewise obtained only in soln.; with Zn dust it gives *1-methyl-3-amino-6-chlorobenzene*, m. $83.5-4.0^\circ$, *aminoditolylamine* (K), prisms from alc.-pentane, m. 121° , and, after oxidation with PbO_2 , *4,4'(?)-dichloro-3,3'-dimethylazobenzene*, yellow needles from AcOH, m. $162-3^\circ$. E, from K with PbO_2 , glassy mass partially decompd. by dil. H_2SO_4 into *m*- $\text{MeC}_6\text{H}_4\text{NH}_2$ and toluquinone. $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{NO}_2$ is obtained in 83% yield from $2,6,4\text{-Cl}_2(\text{O}_2\text{N})\text{C}_6\text{H}_2\text{NH}_2$ in $\text{EtOH-H}_2\text{SO}_4$ at $0-5^\circ$ with AmNO_2 ; reduction with Sn-HCl gives 66% of the NH_2 compd., 12 g. of which in CCl_4 at -20° yields 13 g. $\text{C}_6\text{Cl}_5\text{NH}_2$, silky needles from alc., m. 232° ; this with HOCl in Et_2O yields, almost quant., A, slender, faintly yellowish prisms, m. 111° (decompn.), deflagrates about 130° . B, flesh-colored needles from PhMe, changing after long standing under the solvent at room temp. into deep red tables; both forms begin to turn black-brown at $170-80^\circ$, the original color returning on cooling, m. $317-8^\circ$, dists. with slight decompn. at higher temps.

C. A. R.

An explanation of the Sandmeyer reaction. IVO F. KEMER. *Chem. Ztg.* **46**, 1042 (1922).—The Sandmeyer reaction may be explained upon the assumption that it is the radical attached to the Cu that enters into the ring, and not the acid radical of the diazonium salt. This explains the fact that the Cu salt of the radical which it is desired to introduce into the ring must always be used. The reaction takes place according to the scheme: $\text{CuCN} + \text{PhN}_2\text{CN} + \text{H}_2\text{O} \longrightarrow \text{N}_2 + \text{HCN} + \text{CuOH} + \text{PhCN} \longrightarrow \text{N}_2 + \text{CuCN} + \text{H}_2\text{O} + \text{PhCN}$.

T. S. CARSWELL

Rearrangement of toluene-*p*-sulfonic diphenyl-, phenyl-*p'*-tolyl- and di-*p'*-tolylamide. J. HALBERKANN. *Ber.* **55B**, 3074-95 (1922); cf. *C. A.* **16**, 917.—*4-Methylbenzeno-1-sulfonic acid diphenylamide* (A), $\text{MeC}_6\text{H}_4\text{SO}_2\text{NPh}_2$, obtained by heating Ph_2NH , $\text{MeC}_6\text{H}_4\text{SO}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{N}$ on the H_2O -bath, m. 142° . Heating A with 3 parts H_2SO_4 (d. 1.74) 1st at 140° and then at 125° saponifies it but does not cause rearrangement. The best results are obtained by carrying out the reaction for 4 days at room temp., the product, *p*-tolyl 2-aminophenyl sulfone (B), forming compact prismatic columns, m. $96-7^\circ$. The concd. H_2SO_4 soln. is colorless, but is colored a deep brownish red by a trace of KNO_3 ; solns. in org. solvents have a blue fluorescence. 52% B are obtained, together with 23% Ph_2NH ; the remainder of A is sulfonated. B, treated with NaNO_2 and HCl in dil. AcMe , gives the *nitrosamine* (C), $\text{MeC}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4\text{NPhNO}$, compact prismatic columns, m. $126-7^\circ$. The concd. H_2SO_4 soln. is rose-red, changing to a violet-red; that in $\text{PhOH-H}_2\text{SO}_4$ quickly changes from red to green, then blue and gradually to a deep KMnO_4 color. The *p*-nitroso compound, $\text{MeC}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4\text{NO}$, results upon treating C with alc. HCl ; the salt seps. as ochre-colored compact crystals, m. 197° (decompd.) and is decompd. by shaking with H_2O to give the free base, green prismatic columns with a blue surface luster, m. $150-1^\circ$. Hyposulfite


reduces this to *p*-tolyl 2-4'-aminoanilinophenyl sulfone, compact prismatic columns, m. 134-5°; diazotized, this couples with β -C₁₀H₇OH to give 1-[(2'-*p*-toluenesulfonyl-4'-anilino)benzenazo]-2-hydroxynaphthalene, red needles, m. 172°. The NO compd., boiled with 10% NaOH for 10 hrs., or heated 5 hrs. at 140° in a sealed tube, gave *p*-tolyl 2-aminophenyl sulfone (D), reddish compact glistening prismatic columns, m. 120-1°. Org. solns. have a pale blue fluorescence. The diazo compd., coupled with β -C₁₀H₇OH, gave 1-[2'-*p*-toluenesulfonylbenzenazo]-2-hydroxynaphthalene, large brownish red, glistening prismatic needles, m. 208°. The *o*-position of the NH₂ group in D was established 1st by the synthesis of the *p*-deriv. (Bamberger, *Ber.* 34, 251) from the condensation product of PhMe and AcNHC₆H₄SO₂Cl by sapon. with HCl, and also by the rearrangement of MeC₆H₄SO₂NEtPh with 3 parts H₂SO₄ for 2 hrs. at 100°, giving *p*-tolyl 2-ethylaminophenyl sulfone, compact prisms, m. 90-1°; *N*-acetate, flat, 6-sided needles, m. 141°. D is obtained from this by removal of the Et group (gaseous HCl through the sulfone at 270°). *Toluene-p*-sulfonic acid phenyl-*p*'-tolyl amide (E), glistening needles, m. 122-3°. Rearrangement gave 2 sulfones. *p*-Tolyl 2-4'-methylanilinophenyl sulfone, pale yellow compact prisms or prismatic columns, m. 147°. Alc. FeCl₃ gives a green color. *N*-Acetate, prismatic columns, m. 164-5°. Nitrosoamine, yellow needles, m. 168° (decompn.). PhOH-H₂SO₄ gives a brown color, changing rapidly through brownish red, green to greenish blue; upon warming this changes to a light blue and finally to a brownish red. The sulfone is regenerated by Zn and AcOH, or by HCl-EtOH. Because of the great soly. of the isomeric sulfone, *p*-tolyl 1-anilino-4-methyl-2-phenyl sulfone, it cannot be isolated directly but is obtained through the nitrosamine (F), long 6-sided plates or large rhomboids, m. 132°, by reduction with PhNHNH₂, and forms compact prismatic columns, m. 124°. Zn dust reduces the NO compd. to *N*-phenyl-*N*-[2-*p*-toluenesulfonyl-4-methyl-1-phenyl]hydrazine, (MeC₆H₄SO₂C₆H₄Me)NPhNH₂, compact prisms, m. 169-70°. *N*-Benzal compound, yellowish prisms, m. 195°. F is rearranged by EtOH-HCl to *p*-tolyl 1-4'-nitrosoanilino-4-methyl-2-phenyl sulfone, greenish yellow prismatic columns or needles, m. 174-5°. The hydrochloride forms brownish red compact prisms with greenish blue iridescence, m. 178-9° (decompn.). Reduction of the NO compd. with hyposulfite is difficult because of its slight soly. in NaOH. Reduction with NH₃ and H₂S in MeOH gave the 4'-amine, H₂NC₆H₄NHC₆H₄MeSO₂C₆H₄Me, compact prismatic columns, m. 148-9°. The alc. soln. gives a deep red color with FeCl₃, an aq. soln. a violet-red color. The use of Zn dust for reduction gave bis-[2'-*p*-toluenesulfonyl-4'-methylanilino]-4,4'-azobenzene, also formed by warming mol. amts. of the *p*-NO and *p*-NH₂ compds. in AcOH, small brownish yellow to golden yellow compact prisms, m. 267-8°. The *p*-NO deriv., heated in an autoclave for 5 hrs. at 140° with 10% NaOH, gave MeC₆H₄SO₂C₆H₄MeNH₂. In the rearrangement of E, there is also formed 4-[4'-methyl-2'-*p*-toluenesulfonylanilino]benzene-1-sulfonic acid, isolated as the barium salt, glistening needles, decomp. 269-70°; the alk. soln. is red, the acid soln. blue. The free acid forms glistening microneedles, m. 146° (decompn.). Sodium salt, fine needles. 4-Methylbenzene-1-sulfonic acid di-*p*-tolylamide, MeC₆H₄SO₂N-(C₆H₄Me)₂, compact rhombic plates, m. 144°. Rearrangement gives *p*-tolyl 1-[4'-methylanilino]-4-methyl-2-phenyl sulfone, long pointed needles, m. 110-1°. Nitrosoamine, long 6-cornered plates, m. 148-9°. Zn-AcOH regenerated the sulfone, as does EtOH-HCl. PhOH-H₂SO₄ gives a green soln., changing through deep blue to violet.

C. J. WEST

Oxidation of phenols. VII. The dehydration of *p*-cresol. RUDOLF PUMMERER, DONA MELAMED AND HANS PUTTFARCKEN. *Ber.* 55B, 3116-32(1922); cf. C. A. 14, 69.—0.5 mol. *p*-MeC₆H₄OH in 5 l. H₂O contg. 1 mol. Na₂CO₃. 10H₂O is treated with 1 mol. K₃Fe(CN)₆, giving 46 g. reaction product. In a smaller expt. it was found that 24% of the oxidizing agent was unconsumed. The crude oxidation product was frac-

tionated under 2-3 mm. The 1st fraction consisted principally of p -MeC₆H₄OH. The 2nd fraction, b. 165-75°, contained a small amt. of [Me(HO)C₆H₃]₂, m. 154°, and the *ketone* (A), C₁₁H₁₀O₂, large, rectangular leaflets, m. 124.5°. This may be 2 - p -cresoxy-2,3-dihydro- p -quinomethane, although this is not proved. A is insol. in cold NaOH but dissolves on heating or in concd. EtOH-KOH. Treated with Na in Et₂O, a sodium salt forms, which is yellow and which regenerates A with H₂O. *Benzoate*, m. 153-4°, from the Na salt but not from free A. Titration with Br shows the absence of an enolic form. It couples with p -O₂NC₆H₄N₂OH, giving a brownish red ppt., sol. in alc. KOH with a violet color. It slowly dissolves in NaHSO₃ but does not give a true bisulfite. 90% H₂SO₄ gives a yellow soln., while 75% acid colors the crystals a bright red and then gives a yellow soln. HNO₃ gives an orange-yellow soln., from which H₂O ppts. yellow flakes, sol. in NaOH with a yellowish red color. The *oxime* forms plates, m. 203-4°. The *phenylhydrazone* crystals in long needles, m. 181-2°. *Semicarbazone*, leaflets, m. 249-50°. By means of this insol. compd., it was estimated that the crude reaction product contained 22% A. Under the influence of 70% HClO₄, A rearranges to a *dicresol*, needles, m. 158°. *Dimethyl ether*, compact, glistening prisms, m. 86°, b. 168°. *2-Bromo- p -cresol* (German pat. 156,333) was prepd. from 2,4-H₂N-(HO)C₆H₃Me by the Sandmeyer reaction, long, silk-like spears, m. 54-5°, b. 245-7°. This was transformed into *2- p' -cresoxy- p -cresol*, b₁₂ 200°, m. 33-4°, by heating with p -HOC₆H₄Me, solid KOH and Cu powder at 200-20°. *Urethan*, microneedles, m. 137-75°. *3- p' -Cresoxy- p -cresol*, compact needles, m. 35-7°. *m-Nitrobenzoate*, pale yellow, m. 80°; the crystals are rhombic, bipyramidal, pseudotetragonal, $a:b:c = 0.97:1:0.46$. *p -Cresol- p' -nitrobenzyl ether*, long, pale yellow needles, m. 86-7°. This was reduced to the *p' -amino compound*, m. 110°. *Hydrochloride*, pale yellow. Attempts to eliminate the NH₂ group were not successful. The 3rd fraction of the oxidation product consisted of an isomeric *dicresol*, previously obtained by Fichter (C. A. 14, 1826) by the electrochem. oxidation of p -HOC₆H₄Me, but to which a formula contg. 3 O was given. It really is C₁₁H₁₀O₂; this was confirmed by the analysis of the diacetate. C. J. W.

1,3-Dimethyl-5-hydroxy-4-benzaldehyde, hemellitenol and isopseudocumenol. K. V. AUWERS and K. SAURWEIN. Ber. 55B, 2372-89 (1922).—In connection with a study of the oxidation of *o*-aminophenols (C. A. 15, 3495), hemellitenol, 3,4,5-Me₃C₆H₃OH (A), isopseudocumenol, 2,3,5-Me₃C₆H₃OH (B), and 4,6,2-Me₃(HO)C₆H₃CHO (C), hitherto only difficultly available and hence but little studied, have been more thoroughly investigated. All 3 are obtained from 3,5-Me₂C₆H₃OH (D); unlike Gattermann, who obtained 2,6,4-Me₃(HO)C₆H₃CHO (E) exclusively and almost quant. from D, HCN and AlCl₃ (C. A. 2, 820), v. A. and S. have regularly obtained 8-12% of C also; possibly G.'s reagents were more thoroughly dried, as in 1 expt. in which a little H₂O was introduced accidentally the yield of C was increased to 25%. Reduction of E and C with amalgamated Zn and HCl gives A and B, resp. No smooth oxidation of E and C to the corresponding acids could be effected, nor could C be converted into the acid through the oxime and nitrile, but its Me ether is easily oxidized by KMnO₄ to 1,3-dimethyl-5-methoxy-4-benzoic acid (F), identical with the product obtained by methylation of the known 5-HO acid, m. 166°. With Br under mild conditions, A gives *o,o'*-dibromohemellitenol (G) but attempts to brominate this further generally resulted in more or less carbonization and some unchanged G usually remained: only in 1 of about 8 expts. by heating G with Br in a sealed tube at 100° was there obtained a small amt. of the compd. 2,6,3,5,4-Me₂Br₂(HO)C₆CH₂Br (H), m. 139.5°, identical with the product obtained from 2,6,4-Me₃(HO)C₆H₃CH₂OH (Ann. 344, 271 (1906)). H with hot HNO₃ yields the quinol HO(BrCH₂)₂B₂Me₂Br₂:O (I) which is converted

by alkali into the oxide  CMe₂Br₂:O (J). G with cold concd. HNO₃ yields the

nitroketone or quinitrol $\text{Me(ONO):C}_6\text{Me}_3\text{Br}_2\text{:O}$ (**K**), converted by boiling AcOH into the *quinol* $\text{Me(HO):C}_6\text{Me}_3\text{Br}_2\text{:O}$ (**L**). Unlike most quinitrols, **K** can be kept for a long time without change and is not attacked by H_2O , alc., $(\text{NH}_4)_2\text{S}$, etc., in the cold, nor by long boiling with MeOH; alkalis act upon it, to be sure, but only gradually. **L** is only weakly acid; concd. H_2SO_4 converts it into a high-melting compound (**M**), whose nature has not been established owing to lack of material. **A** is not attacked by cold HNO_3 ; only when heated to incipient boiling does it yield the quinitrol $\text{Me(ONO):C}_6\text{Me}_3(\text{NO}_2)_2\text{:O}$ (**N**), converted by moderate heating with AcOH into the *quinol* (**O**). With Ca(OH)_2 or Ba(OH)_2 as condensing agents, **A** with HCHO yields the compd. $3,4,5,6\text{-Me}_4(\text{HOCH}_2)_2\text{C}_6\text{OH}$ (**P**) changing on longer continued action into a substance (**Q**) m. above 360° ; in the presence of NaOH there are formed, depending on the conditions, either the pure **P** or **Q** or mixts. of the two. With HBr in AcOH **P** yields the dibromide (**R**), which cannot be reduced in Et_2O with Zn and HCl to $\text{C}_6\text{Me}_3\text{OH}$, **P** always being regenerated. Coupling of **A** with PhN_2Cl in NaOH of varying concn. always gives only the monoazo compd. (**S**), which seps. immediately and thus escapes further attack. **B**, on the other hand, regularly gives mixts. of the mono- and disazo compds., the amt. of the latter increasing with the concn. of the alkali. On cautious treatment with HNO_3 in AcOH **B** gives exclusively the *o*-compd. $2,3,5,6\text{-Me}_4(\text{O}_2\text{N})\text{-C}_6\text{HOH}$ (**T**). Semicarbazone of **C**, fine powder from AcOH, m. 240° ; phenylhydrazone, flat needles from light benzine, m. $126.5\text{--}7.0^\circ$; *anti*, yellow silky needles from MeOH or EtOH, m. $88.5\text{--}9.0^\circ$; *oxime*, fine, silky needles from dil. alc., m. $125\text{--}6^\circ$, gives a red-violet color with FeCl_3 , is easily converted back into **C** by boiling with 1:1 HCl; methyl ether, long, fine needles from MeOH, m. $48\text{--}9^\circ$, gives with alk. KMnO_4 60% of **F**, platelets, m. $167.5\text{--}8.0^\circ$, whose methyl ester b. $261\text{--}3^\circ$. 1,3-Dimethyl-5-hydroxy-4-benzonitrile, fine needles with a faint PhOH odor from H_2O , m. $177\text{--}8^\circ$, obtained through the acetate, flat, dull needles, m. $49\text{--}50^\circ$, by boiling the oxime of **C** with Ac_2O and NaOAc. 1,3-Dimethyl-5-hydroxy-2-benzeneazo-4-benzaldehyde, brownish leaflets with dull luster from AcOH or MeOH, m. $97.5\text{--}8.0^\circ$, sol. in NaOH with red color. **A**, obtained in 40% yield from 30–40 g. **E**, finely rubbed up with concd. HCl, added in the course of 2 hrs. to 150–200 g. amalgamated Zn and 300–400 g. of boiling 1:1 HCl and boiled about 6 hrs., long, felted needles with faint bluish fluorescence from light benzine, m. 107° , gives no color with FeCl_3 . **G**, best prepd. by adding **E** to an excess of ice-cold Br until the product forms a spongy mass and letting the excess of Br evap. in the air, leaflets from dil. alc., m. $142.5\text{--}3.0^\circ$. Tribromomethylitylquinol (1,3-dimethyl-2-bromomethyl-2-hydroxy-4,6-dibromocyclohexa-3,6-dien-5-one) (**I**), fine felted needles from C_6H_6 , m. 213° , sol. in aq. alkalis only on warming; on addn. of dil. NaOH to permanent alk. reaction to a MeOH soln. (treated to incipient turbidity with H_2O), it gives **J**, fine, soft leaflets from heavy benzine, m. $156\text{--}60^\circ$ (decompn.), gradually turns brown on long heating on the H_2O bath. Dibromomethylitylquinitrol (**K**), monoclinic leaflets from Et_2O , m. 108° (evolution of N oxides), decomp. on boiling in solvents which b. above 70° ; boiled 1–2 min. in AcOH it gives 85% of **L**, long, fine needles, m. $214\text{--}5^\circ$. Dinitromethylitylquinitrol (**N**), obtained in about 60% yield; fine needles, m. $146\text{--}7^\circ$ (gas evolution), slowly decomp. in the air and in contact with alkalis, evolves N oxides on boiling in solvents which b. above 60° , converted by heating in AcOH about 5 hrs. at 50° into **O**, fine needles from AcOH or C_6H_6 , m. 213° , sol. in alkalis with faint yellowish color, reprecip. unchanged by acids. *o,o'*-Dimethylolhemitenol (**P**), felted needles from benzene, m. 148° , gives a deep pure blue color with FeCl_3 . 2',6'-Dibromopentamethylphenol, $\text{Me}_2(\text{BrCH}_2)_2\text{C}_6\text{OH}$ (**R**), short needles from light benzine, m. $164\text{--}5^\circ$, insol. in alkali. *o*-Benzeneazohemitenol (**S**), fine, brown-red needles with faint blue surface luster from MeOH or EtOH, m. $126.5\text{--}7.0^\circ$, insol. in alkalis. **B** is obtained in 40% yield from **C**. *o*-Nitroisopseudocumenol (**T**), obtained in 60% yield from 2 g. **B** in AcOH slowly treated

with 1 cc. concd. HNO_3 , light yellow leaflets from alc., m. $78-9^\circ$, sol. in alkalis with dark red color. *p*-Benzeneazoisopseudocumenol, bright red, flat needles from benzene, m. $154.5-6.5^\circ$, is the chief product when the coupling is carried out in 2% NaOH; in 4% NaOH is obtained the *o,p*-disazo compound, brown crystals from AcOH, m. $130.5-1.5^\circ$. C. A. R.

Bases obtained in the decomposition of azides of the thiocarbamic acids. E. OLIVERI-MANDALÀ. *Gazz. chim. ital.* 52, II, 98-103(1922).—From HNO_3 acting on aliphatic thiosemicarbazides Freund and Schwarz (*Ber.* 29, 2491 (1896)) obtained derivs. of triazosulfole (A), $-\text{NC.N.N.N.S}$. From corresponding aromatic derivs. tetrazole derivs. (B), $-\text{SC.N.N.N.N-}$, are obtained. Recently O.-M. (*C. A.* 9, 71) detd. that these compds. are derivs. of azides of thiocarbamic acid, $-\text{NHC}(:\text{S})\text{N.N}$ or $-\text{NH.C-}$

$(:\text{S})\text{N:N:N}$. A with dil. H_2SO_4 or boiled with H_2O decoups., giving 2 atoms N and 1 atom of S. With concd. boiling HCl 2 atoms N are evolved and hydrochlorides (C) of RNHC.N.S or RN:C.NH.S are formed. If R is an aromatic group the free bases of C can be obtained. These bases (D) resemble the nitrile oxide (E) of Wieland (*C. A.* 4, 330) in structure and in their genesis (cf. also Schroeter, *C. A.* 3, 2555). This resemblance also extends to the tendency of these bases to polymerize but unlike E they lose S on boiling in H_2O , dil. acids or org. solvents, giving the corresponding cyanamide derivs. as polymers, $(\text{RNHCN})_n$. D may also have an open structure, RNH.C:N:S , i. e., may be derivs. of the hypothetical HC:N:S , which harmonizes better with their behavior. Accordingly PhNHCN:S should be called anilinesulfonitrile instead of phenylthiocyanamide. *o*-Toluidinesulfonitrile (F) was obtained by long boiling of the corresponding azide (*C. A.* 16, 562) in concd. aq. HCl and neutralizing the soln. with alkali. The F crystd. from EtOH, m. $138-40^\circ$, gave a mol. wt. of 200 (calcd. 164) in freezing glacial AcOH, gave a hydrochloride, $\text{C}_6\text{H}_5\text{SN}_2\text{HCl}$, which was pptd. with EtOH; the chloroplatinate, $(\text{C}_6\text{H}_5\text{SN}_2\text{HCl})_2\text{PtCl}_4$, sep'd. at once as a yellow ppt. *p*-Toluidinesulfonitrile (G) was obtained like F; its hydrochloride was pptd. on passing HCl into a soln. of G; its chloroplatinate was pptd. as a fine, white powder. Anilinesulfonitrile (H) (previously described, O.-M. *C. A.* 9, 71) gave a mol. wt. of 181 (calcd. 150) in glacial AcOH; its hydrobromide was obtained by evapg. the HBr soln. of H over KOH *in vacuo*; its chloroplatinate was obtained as usual. 10 g. EtNCS in concd. Et₂O soln. with excess HN_3 gave, on standing some days in the cold, the corresponding azide (I), EtNHCSN_3 , m. 66° , which was pptd. with petroleum ether. Attempts to realize the reaction $\text{RNHCSN}_3 + \text{HgO} \rightarrow \text{HgS} + \text{RNHCN}$ with I failed but gave an addition product of H_2O with I. I boiled with concd. HCl gave ethylaminesulfonitrile (J), EtNHCSN , as the hydrochloride which was pptd. as the chloroplatinate. The free base of J could not be isolated because of its instability.

E. J. WITZEMANN

Azopicric acid (2,2',4,4',6,6'-hexanitro-5,5'-dihydroxyazobenzene). K. ELBS AND FR. SCHLIEPHAKE. *J. prakt. Chem.* 104, 282-4(1922).—The attempts to prep. azopicric acid (A) by nitration of *m*-azoaniline and subsequent electrolytic reduction were not successful (cf. Elbs and Kopp, *Z. Elektrochem.* 5, 110 (1898-9); Elbs and Kirsch, *J. prakt. Chem.* 67, 266(1903)). These results will be published later. A was prepd. by adding slowly with stirring 12 g. NaNO_3 and 60 cc. concd. H_2SO_4 to 4 g. *m*-azophenol cooled with ice, allowing to stand 3 hrs. at room temp., pouring into 1 l. H_2O and extg. with PhH ; a double compd. of A and 2 mols. PhH seps. on partial evapn. of the soln.; the red crystals lose PhH at $80-90^\circ$, giving pure A (yield 60%); when slowly heated it m. $238-9^\circ$; it is readily sol. in H_2O , EtOH, Et₂O or Me_2CO , fairly sol. in PhH , forming

a double compd. insol. in CS_2 or concd. HCl ; **A** and its salts explode when heated rapidly; **A** is a strong acid, forming colored salts; aq. solns. dye wool; a potassium salt forms red leaflets and is fairly sol. in H_2O ; barium salt ($4\text{H}_2\text{O}$), forms dark red leaflets.

N. A. LANGE

Valence problem of sulfur. VII. *o*-Nitrophenyl dithiochloride. HANS LECHER AND KURT SIMON. *Ber.* 55B, 2423–32(1922); cf. *C. A.* 16, 181.—The problems of diazo chemistry have been approached from an entirely new direction by substituting another metalloid, S, for the diazo N. The *o*-nitrophenyl dithiochloride, $\text{O}_2\text{NC}_6\text{H}_4\text{SSCl}$ (**A**), unlike PhN_2Cl , is not a salt, as it is a non-conductor in $(\text{CHCl}_3)_2$; with this observation disappears all basis for formulating **A** as a heteropolar “dithionium chloride,” $(\text{ArS:S})^+\text{Cl}^-$. “Diazo cleavages” are facilitated by the fact that the diatomic N mol. is already prepd. in the aromatic diazo compds. As such a “preparation” of the S mol. does not occur in the aryl dithiochlorides, analogous reactions in the S series are, *a priori*, not to be expected, but the difference from N compds. is not limited to the failure of such reactions, in which both S atoms are split off together in elementary form; in the S series the S : S union is easily ruptured by double decompn., especially by alk. hydrolysis; thus, *e. g.*, **A** + 2KOH gives $\text{O}_2\text{NC}_6\text{H}_4\text{SK}$ + (HOSOH) + KCl, a reaction which has no analog in aromatic diazo chemistry. With H_2O instead of alkali, there is apparently hydrolysis only of the S-Cl union, with formation of the *o*-nitrophenyl dithiooxide ($\text{O}_2\text{NC}_6\text{H}_4\text{SS}_2\text{O}$) (**B**), which, on account of its instability, could not be isolated pure. It is concluded that the S atom in **A** which on alk. hydrolysis is eliminated as HOSOH plays the role of a positive mol. constituent combined with the negative Cl on the one side and the mercaptan residue on the other and that the aryl dithiochlorides belong to the relatively small class of sulfides in whose reactions bivalent S functions as a positive element without its unions being heteropolar and ionogenous. To this class belongs SCl_2 ; **A** may be considered as SCl_2 in which one Cl atom is replaced by $\text{O}_2\text{NC}_6\text{H}_4\text{S}$, and *o,o'*-dinitrodi(phenyl trisulfide) (**C**), which may be regarded as SCl_2 in which both Cl atoms are so replaced, is hydrolyzed by alkali to $\text{O}_2\text{NC}_6\text{H}_4\text{SK}$ and HOSOH. In view of the above differences between aromatic diazo and dithio compds., it can no longer be considered as a formal analogy that both types of compds. couple, for besides the aromatic diazo compds. there are many substances with easily mobile negative groups which couple. *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{SH}$ is obtained in 60% yield from 30 g. powdered $(\text{O}_2\text{NC}_6\text{H}_4)_2\text{S}_2$ and 21 g. glucose allowed to stand overnight in 100 cc. of 95% alc., treated at 60–70° with 16 g. NaOH in 30 cc. H_2O in 5 cc. portions, poured warm into 400 cc. H_2O and filtered into 75 cc. concd. HCl and ice; it seps. from CCl_4 -petr. ether (1:2) in hard, yellow crystals, m. 57–8°, which should dissolve clear in Et_2O with yellow, in aq. NH_4OH with red color; in well stoppered bottles it is stable indefinitely; in the air it oxidizes slowly in solid form, rapidly in alk. soln., to the disulfide. **A** is apparently stable for a long time at room temp. in sealed tubes; a cold satd. ligroin soln. also changes but little on boiling 3 hrs.; heated without a solvent it darkens about 100°, evolves S_2Cl_2 at 150° and deflagrates above 200°. *p*-Dimethylaninophenyl *o*-nitrophenyl disulfide (2.5 g. from 3.6 g. PhNMe_2 and 2.2 g. **A** refluxed 15 min. in Et_2O), orange tables from alc., m. 115.5–7.0°, sol. in dil. HCl, is not thermochromic. **C** (3.15 g. from 2.2 g. **A** and 1.6 g. $\text{O}_2\text{NC}_6\text{H}_4\text{SH}$ in Et_2O), yellow needles, m. 174.5–6.0° (Blanksma, *Rec. trav. chim.* 20, 144(1901), gives 185°; it is doubtful if his product was pure), sol. in KOH in cold MeOH and in hot aq. KOH with red color, decomp. on long boiling in xylene. With piperidine **A** gives piperidine-HCl and a reddish yellow oil, the amt. of which corresponded to that calcd. for the mixed disulfide but which could not be distd. or crystd. without decompn.

C. A. R.

Orcinol: its properties, derivatives, and history. JOHN MISSENDEN. *Chem. Age* (London) 7, 709(1922).—The most sensitive test for orcinol is the bright red color,

changing to green upon diln. with H_2O , obtained by heating the suspected substance with $CHCl_3$. It exists in lichens, and may be prepd. by crushing 5 parts of *Rocella fuiformis* with 55 parts of Ca lactate and 2 parts of CaO, and filtering the resulting mush. The erythrin is pptd. from the filtrate by HCl and heated with an alkali, when orcinol is formed.

T. S. CARSWELL

$\alpha, \alpha, \beta, \beta$ -Tetrasubstituted propiophenones and their action with sodium amide. GEORGES ALBESCO. *Ann. chim.* 18, 216-62(1922); cf. *C. A.* 16, 2495.—Employing $NaNH_2$, Haller (*C. A.* 5, 3227; 7, 3311) obtained hexaalkylated aliphatic ketones and trialkylated mixed ketones, which reacted with excess $NaNH_2$ as follows: (a) $R_1R'_1R'_2R'_3CCOCR_2R_3R_4 + NaNH_2 = R_1R_2R_3CCONHNa + CHR_1R_2R_3$; (b) $PhCOCR_1R_2R_3 + NaNH_2 = R_1R_2R_3CCONHNa + C_6H_5$ ($R_1R_2R_3$ being light radicals); (c) $PhCOCR_1R_2R_3 + NaNH_2 = PhCONHNa + CHR_1R_2R_3$ ($R_1R_2R_3$ being heavy radicals). A. studied $\alpha, \alpha, \beta, \beta$ -tetrasubstituted propiophenones, $R_1R_2CHCR_3R_4COPh$ (Z), R_2 and R_4 being aliphatic, R_1 aromatic and R_3 aliphatic or aromatic. The substitution in the β -position was effected by the action of $RMgX$ on unsatd. α, β -ketones, that in the α -position by the Haller procedure with $NaNH_2$. The second substitution in the α -position is difficult owing to a splitting of the mol. to give a hydrocarbon and $BzNH_2$. With $NaNH_2$, type Z splits in two manners, one giving tetrasubstituted $EtCONH_2$ and C_6H_6 , the other tetrasubstituted C_2H_2 and $BzNH_2$. The following β, β -disubstituted propiophenones were prepd.: *Diphenyl* (A), made by the method of Kohler (*Am. Chem. J.* 31, 649). *Phenyl-p-tolyl* (B) was prepd. by first mixing 12.7 g. Mg and 80 g. *p*- MeC_6H_4Br in 100 cc. anhyd. ether, cooling to -10° after the formation of the organo-metallic compd. and adding dropwise 80 g. $PhCH:CHCOPh$ in ether, then heating for 2 hrs. The product was decompd. by ice mixed with NH_4Cl , the ether soln. washed, dried with Na_2SO_4 , and distd. The residual oil, recrystd. from alc., gave crystals of the ketone, m. 96° , b_{12} 254° , sol. in C_6H_6 , ether, less sol. in alc. *Phenylanisyl* (C), crystals (from alc.-ether), m. 93° , b_{14} $275-80^\circ$, from $MeOC_6H_4MgBr$ and $PhCH:CHCOPh$, prepd. by Kohler (*C. A.* 2, 824) from $PhMgBr$ and $MeOC_6H_4CH:CHCOPh$. *Phenylethyl* (D), b_{14} 185° , crystals from abs. alc. m. 58° , very sol. Oily condensation products were also obtained. *Methylenedioxyphenylmethyl* (E), prisms from ether, m. 73° , b_{10} 240° , sol. in alc., C_6H_6 , and ether. *Methylenedioxyphenylethyl* (F), prisms from alc.-ether, m. 58° , b_{11} 233° . *Phenylmethylenedioxyphenyl* (G), crystals from ether, m. 97° , b_{14} 280° , sol. in C_6H_6 and alc. The β, β -substituted ketones were then transformed into the following β, β, α - and $\beta, \beta, \alpha, \alpha$ -substituted propiophenones by employing $NaNH_2$. β, β -*Diphenyl- α -methyl* (H), obtained by heating 150 g. anhyd. thiophene-free C_6H_6 , 75 g. A, 13.5 g. powdered $NaNH_2$ in a flask fitted with a reflux condenser and separatory funnel until the evolution of NH_3 was almost complete, or about 4 hrs., cooling, adding 55 g. MeI, letting stand 1 hr., then heating, cooling again, adding distd. water slowly, washing the C_6H_6 layer with water, drying with Na_2SO_4 , and distg., prisms from alc.-ether, m. $102-3^\circ$, b_{14} 254° , prepd. by Kohler from $PhMgBr$ and $PhCH:CMCOPh$, m. 105° . β, β -*Diphenyl- α, α -dimethyl* (I), obtained in 40% yield by methylating H, crystals from alc., m. 90° . The mother liquors contained unaltered H and products of decompn. β, β -*Diphenyl- α -ethyl* (J), m. 118° , from alc.-ether, by ethylating A. β -*Phenyl- β -ethyl- α -methyl* (K), crystd. in a freezing mixt., m. $54-5^\circ$, b_{14} 194° , sol. in ether, C_6H_6 , alc., less so in ligroin, obtained by methylating D. β -*Phenyl- β -ethyl- α, α -dimethyl* (L), by methylating K, viscous oil, b_{10} 187° ; there was also obtained by decompn., $PhCHI_2$, liquid of agreeable odor, b. 195° . β -*Phenyl- α, β -diethyl* (M), by ethylating D, b_{15} 200° , needles from alc., m. 68° . Condensation of benzylidenecyclopropenone with $EtMgBr$ gave the same compd. β -*Phenyl- α, α, β -triethyl* (N), by ethylating M, viscous oil, b_{10} 180° ; there is also obtained a hydrocarbon, b. 195° , produced by splitting the mol. β -*Phenyl- β -p-tolyl- α -methyl* (O), by methylating B, crystals

from alc. m. 116°, slightly sol. in ether and ligroin. β -Phenyl- β -*p*-tolyl- α -ethyl (P), by ethylating B, b₁₂ 252°, crystals from alc.-ether, m. 131°, slightly sol. in ligroin, sol. in alc., ether, and C₆H₆. β -Phenyl- β -methoxyphenyl- α -methyl (Q), by methylating C, oil crystd. out of alc., m. 128°, sol. in hot alc., slightly sol. in ether and ligroin. β -Methylenedioxyphenyl- α , β -dimethyl (R), by methylating E, b₁₁ 220°, crystd. out of ether or ligroin on cooling, m. 70°, very sol. in ether and C₆H₆, less sol. in alc. and ligroin. β -Methylenedioxyphenyl- α , α , β -trimethyl (S), by methylating R, viscous oil b₁₃ 231°; there was also obtained a hydrocarbon, liquid of agreeable odor, b. 230°. β -Methylenedioxyphenyl- β -ethyl- α -methyl (T), by methylating F, oil b₁₆ 236°. β -Methylenedioxyphenyl- β -ethyl- α , α -dimethyl (U), by methylating T, b₁₁ 235°, impure; there was also obtained a hydrocarbon, liquid, b₁₁ 200°. β -Methylenedioxyphenyl- α , β -diethyl (V), by ethylating F, odorless oil, b₁₃₋₁₄ 234-5°. β -Methylenedioxyphenyl- α , α , β -triethyl (W) was not obtained pure. β -Methylenedioxyphenyl- β -phenyl- α -methyl (X), by methylating G, needles from alc.-ether, m. 128°. The action of the tetrasubstituted ketones with an excess of NaNH₂ was then studied. A mixt. of 10 g. powdered NaNH₂, 31 g. I, and 100 g. anhyd. xylene was refluxed for 5 hrs., cooled, and water added. α , α -Diphenyl- β -methylpropane, practically odorless liquid, b₁₃ 145°, and impure β , β -diphenyl- α , α -dimethylpropionamide, m. 118-120°, were obtained by distn. of the xylene layer. BzNH₂ was identified in the residue by its m. p. and sapon. to BzOH. The impure amide was sapon. and the acid reconverted into the amide by SOCl₂ and Et₃O-NH₃ soln. The pure amide forms white needles, m. 122°, from ether-ligroin mixt. β , β -Diphenyl- α , α -dimethylpropionic acid was also obtained mixed with BzOH in the water layer. Purified through its Na salt, it gave large crystals, m. 134°. Tetraphenylethane, m. 208°, was obtained by filtration of the xylene layer. Its formation is attributed to condensation of Ph₂CH residues. The action of NaNH₂ on L produced 2-methyl-3-phenylpentene, odorless liquid, b. 200°, and β -phenyl- β -ethyl- α , α -dimethylpropionamide, viscous yellow liquid, b₁₁ 180° (purified by sapon. and reversion). β -Phenyl- β -ethyl- α , α -dimethylpropionic acid, crystals from ligroin, m. 82°. The action of NaNH₂ on N produced 3-phenyl-4-ethylhexane, liquid of agreeable odor, b. 205°, and, by sapon. of the impure amide, β -phenyl- α , α , β -triethylpropionic acid, crystals from ether-ligroin, m. 68-9°. NaNH₂ heated in xylene with J for 5 hrs. gave β , β -diphenyl- α -ethylpropionamide, crystals from alc., m. 151°, sol. in alc. and ether and 2,2-diphenylbutane, liquid with a hydrocarbon odor, b₁₄ 152°; some J was recovered, and BzNH₂ was identified by conversion to BzOH. At the b. p. of xylene the α -monosubstituted ketones decompd. with NaNH₂ in a manner analogous to the α , α -disubstituted compds. A. C. PURDY

Amino alcohols. Homologs of novocaine. F. FOURNEAU AND J. PUYAL. *Anales soc. españ. fis. quim.* 20, 207-20 (1922).—3-Dimethylamino-2-propanol (A), MeCH(OH)-CH₂Me, was prepd. by heating 12 g. MeCH(OH)CH₂Br (B) and 65 cc. of 20% Me₂NH in C₆H₆ in a sealed tube for 6 hrs. at 125° (yield, purified, 6 g.), b₂₅ 45°. 3-Diethylamino-2-propanol (C), readily prepd. from B and Et₂NH in C₆H₆, b. 157°. 3-D-methylamino-2-butanol (D), prepd. from the bromohydrin, chlorohydrin, and oxide of dimethylethylene by heating with Me₂NH in C₆H₆, b. 145°, b₁₈ 53°. 3-Diethylamino-2-butanol (E), from the bromohydrin and Et₂NH, b. 167-72°, b₁₈ 74°. In like manner were prepd. dimethylaminodimethylethylcarbinol [1-dimethylamino-2-methyl-2-butanol] (F), and the diethylamino compound (G), b₃₀ 94°. By adding 3 g. A to 5.4 g. O₂NC₆H₄COCl (H) in PhH was obtained 7 g. of 3-dimethylamino-2-propanol *p*-nitrobenzoate hydrochloride, crystals from abs. EtOH, m. 198°. *p*-Nitrobenzoate hydrochloride (K) of C, m. 187°, was prepd. in like manner. *p*-Aminobenzoate hydrochloride of C, methylnovocaine (L), prepd. by reduction of K by Sn and HCl, crystals from abs. EtOH-Et₂O, m. 150-2°. Placed on the tongue it appears to be more anesthetic than novocaine. *p*-Nitrobenzoate hydrochloride (M) of E, prepd. by mixing

concd. PhH solns. of **E** and **H**, seps. after standing for some time as an oil which slowly crystals; recrystd. from abs. EtOH, *m.* 148°. On the tongue it gives a bitter, cooling taste and a slight anesthetic effect. Amino compound-HCl, dimethylnovocaine (**N**), by reduction of **M**, crystals from abs. EtOH, *m.* 172°. On the tongue it is slow to produce an anesthetic effect but the effect is more intense and lasts longer than that produced by novocaine. Attempts to make the derivs. of **D** corresponding to **M** and **N** were abandoned because the compds. were difficult to cryst. *p*-Nitrobenzoate hydrochloride (**O**) of **F**, prepd. by mixing mol. amts. of **F** and **H** in PhH, yellowish needles, *m.* 184°, very bitter, slightly sol. in acetone, less sol. than stovaine in H₂O and EtOH. Amino compound, aminostovaine or ethylmethylnovocaine, was prepd. by reduction of **O** with Sn and HCl. The free base is very sol. in PhH and EtOH and forms needle-like crystals, *m.* 73°. The HCl salt is very hygroscopic and difficult to cryst. Its aq. soln. is neutral to litmus. KI added to the soln. slowly ppts. the HI compd. This can be recrystd. from hot H₂O, *m.* 159° and has a very intense anesthetic effect on the tongue.

L. E. GILSON

The sulfophthalic acids and their salts. JOHN MISSENDEN. *Chem. News* 125, 328-30 (1922).—*α*-Sulfophthalic acid or the 1,4,2-acid with 1 H₂O, *m.* 148° and forms an anhydride at 167°. *ν*-Sulfophthalic acid or the 1,3,2-acid prepd. by oxidation of *α*-C₁₀H₇SO₂NH₂ with KMnO₄ is sol. in H₂O. Normal barium *α*-sulfophthalate (**B**) with excess HCl forms the *diacid salt*, Ba[C₆H₃(CO₂H)₂SO₃]₂·5H₂O; 2 parts **B** and 3 parts HCl give the *monoacid salt*, C₆H₃(CO₂BaSO₃)CO₂H·2H₂O. Normal barium-*ν*-sulfophthalate with 8 H₂O has properties similar to **B**. Ammonium-*α*-sulfophthalimide, which is prepd. by heating the monoacid NH₄ salt, decomps. at higher temps. to phthalimide, NH₃, SO₂ and H₂O. Sulfonidephthalic acid (**C**), C₆H₃NSO₃·2H₂O, is dibasic; alkalis do not convert it to sulfamicphthalic acid; at 162° it becomes anhydrous; the *dimethyl ester* (**D**) of **C** is sol. in EtOH, insol. in H₂O, *m.* 173°; the *dipotassium salt* is sol. in H₂O; the *monosilver salt* with 1 H₂O is sol. in hot KNO₃ soln. and insol. in H₂O; the *monomethyl ester* of **C**, *m.* 192.3° and forms **D** with PCl₅ and MeOH; the *monopotassium salt* with 1 H₂O becomes anhydrous at 103°. *α*-Sulfamidophthalic acid, C₆H₃(SO₂NH₂)(CO₂H)₂ with PCl₅ gives the monochloride, C₆H₃(SO₂Cl)(CO₂H)₂ which is converted to the *amide* with NH₃. Potassium hydrogen sulfonidephthalate (**E**) is more sol. in hot than in cold H₂O; AgNO₃ added to a hot soln. of **E** gives the *silver hydrogen salt*, C₆H₃N-SO₃Ag·H₂O, which loses H₂O at 131.5°.

N. A. LANGE

The configuration of β-phenylglyceric acids and of phenylglycidic acid. J. BÖSEKEN WITH C. DE GRAAFF. *Rec. trav. chim.* 41, 199-207 (1922).—The racemic β-phenylglyceric acids and their optical components are all known (Rüber, Berner, *C. A.* 12, 691) but their configuration is not certainly known because Böseken and Derr (*C. A.* 15, 3629, 3631) found reversion during the oxidation of cinnamic acid by KMnO₄. When the projections of the 2 isomers on a plane are considered it is obvious that H₂BO₃ may exercise a greater influence on the acid (**A**) in which 2 OH groups appear on one side of the figure (*m.* 120°). It was found however that the increase in cond. is greater with the other form (**B**) (*m.* 141°), which conforms with the formulas previously proposed and shows that the 2 OH groups are added to the C₂H₅ function of cinnamic acid without reversion. Although this conclusion is not general it is true that KMnO₄ oxidation gives the *cis*-form almost exclusively (cf. *C. A.* 12, 2545; 13, 332). **A** was also obtained by the hydration of phenylglycidic acid (**C**), which was obtained thus: PhCH=CHCO₂Na with HOCl gives PhCH(OH)CHClCO₂Na (**D**) and this with 2 equivs. NaOH gives **C**. On acidifying **C** is largely decompd. into CO₂ + PhCH₂CHO and some **A**. The configuration of **C** and **D** could not be detd. with certainty because of 2 opportunities for reversion in the prepn. of **A**. van Loon found that the hydration of indene oxide gives mainly *cis*-hydrindene-1,2-diol in slightly acid soln.

while in alk. soln. the *trans*-form is the main product. The same holds true for C. When the K or Na salts of C are decompd. by dil. H_2SO_4 , B is formed but after boiling some hrs. with excess of OH^- A is obtained. From the configuration of B it is deduced that in C the Ph and CO_2H are *trans* to the triatomic ring. A and B have nearly the same dissociation const. while the difference due to increase with H_3BO_3 exceeds 10000 Kohlrausch-Holborn units, which shows that this influence is not due to acidity itself. The dissoc. consts. of A and B are 2.35×10^{-4} and 2.54×10^{-4} , resp. It is probable that the Ph and CO_2H groups are closer together in B than in A. E. J. W.

Gallic aldehyde and its derivatives. K. W. ROSENMUND AND E. PFANNKUCH. *Ber.* **55B**, 2357-72 (1922).—In the prepn. of gallic aldehyde (A) by the catalytic reduction of triacetylgalloyl chloride (B) (C. A. **12**, 2659), the intermediate *triacetylgallic aldehyde* (C) can be isolated if very pure reagents and catalysts are used. C is characterized by an extraordinary inertness so that it is of no use for syntheses, but its hydrolysis yields very pure A. Attempts to prep. *gallyl alcohol* (D) by catalytic reduction of A gave a product (E), the mol. wt. of whose Ac deriv. indicates that during the reduction about 6 mols. A condense with each other. It was next sought to prep. D from *gallylamine* (F) which, like *digallylamine* (G) and the Ac derivs. of F and G, contracts the isolated guinea pig uterus very powerfully. C, obtained in about 90% yield in 2-2.25 hrs. from 3.6 g. B and 1 g. catalyst in 17 cc. boiling xylene with H, m. $107-8^\circ$, mol. wt. in boiling Me_2CO 270-308; *p*-nitrophenylhydrazone, pure yellow, slender, rhombic platelets or, on very rapid cooling, long needles from 90-100% AcOH, m. $207-8^\circ$ (slight decompn.), sol. in alkalies, especially alc., with violet color. No other deriv. of C could be obtained. Hydrolysis with boiling alc. KOAc gives about 85% A. *Tribenzoyl gallic aldehyde*, from A benzoylated in H by the Schotten-Baumann method, is a sticky, viscous, yellowish brown mass whose *p*-nitrophenylhydrazone, pure yellow, indistinctly cryst. flocks from PhMe-petr. ether, m. $232-3^\circ$ (decompn.). A has a mol. cond. of 1.25 at 19.8° for V 64, whence, contrary to an earlier observation that it must be a stronger acid than AcOH, it is weaker than AcOH (12.9 at 25° , V 64) but twice as strong as pyrogallol (0.64 at 25° , V 52). *Triacetyl gallic aldehyde diacetate*, $(\text{AcO})_3\text{C}_6\text{H}_2\text{CH}(\text{OAc})_2$, from A, excess of Ac_2O and a little $\text{C}_6\text{H}_5\text{N}$ gently warmed 5-10 min., fern-like leaflets from 50% AcOH, m. 166° , slowly sol. with strong discoloration in hot NaOH. *Gallic aldoxime*, obtained in 92% yield, rectangular tablets with 1 H_2O , darkens about 160° , decomp. $195-200^\circ$, gives in H_2O with FeCl_3 the tannin reaction and with KCN a violet-red color; covered with twice the calcd. amt. of Ac_2O and $\text{C}_6\text{H}_5\text{N}$ and poured into cold H_2O after 15 min. it gives almost quant. *triacetyl gallic aldoxime acetate*, m. $126-7^\circ$. *3,4,5-Trihydroxy- ω -nitrostyrene*, obtained in 60% yield from 1 g. A, 0.5 g. MeNO_2 , 3 drops concd. aq. MeNH_2HCl and a little Na_2CO_3 in alc. allowed to stand 7-8 hrs. in a closed flask, reddish yellow needles or red rods with 1 H_2O from alc. or Me_2CO and H_2O ; begins to decomp. about 160° , decomp. completely $180-5^\circ$, sol. in alkalies with an intense red color soon assuming a dirty shade. *p*-Acetoxy- ω -nitrostyrene, from the HO compd. and Ac_2O gently warmed in $\text{C}_6\text{H}_5\text{N}$, long faintly yellow needles from alc., m. 163° . *3,4-Diacetoxy- ω -nitrostyrene*, yellowish needles, m. 127° . *3,4,5-Triacetoxy- ω -nitrostyrene*, needles, m. 183° . From 0.36 g. of the oxime of A and 0.3 g. Pd-BaSO₄ in H_2O suspension shaken 20 min. in H and then treated with the calcd. amt. of HCl is obtained the *hydrochloride*, m. $208-10^\circ$, gives an indistinct, evanescent, dirty blue-green color with FeCl_3 , of G which was not obtained pure but is pptd. by the calcd. amt. of alkali, quickly turns deep brown in the air, does not react alk. in H_2O suspension but redissolves in HCl. *Triacetyl gallylamine hydrochloride*, obtained in 75-80% yield from 0.654 g. $(\text{AcO})_3\text{C}_6\text{H}_2\text{CH}\cdot\text{NOAc}$ and 0.5 g. catalyst in AcOH suspension shaken 10 min. with H, rosetts of needles from EtOH + 2 vols. xylene, m. $196-7^\circ$ (foaming), gives no FeCl_3 reaction, hydrolyzed by heating 10 min. on the H_2O

bath with 4 mols. of 3.8% HCl to the *hydrochloride* of F, cryst. warts from MeOH-Et₂O, m. 225-6° (decompu.), gives with FeCl₃ a blue color with a faint violet tone, with KCN an orange-yellow color; the free F could not be isolated. From 0.5 g. A in 3 cc. alc. added to 0.4 g. methylketole in 3 cc. satd. alc. HCl is obtained 3,4,5-trihydroxy-phenyl[α -methyl- β -indolylene]methane hydrochloride, yellow-red needles from dil. HCl, darkens about 140°, decomps. 170°; with chloranil in alc. with a little HCl it gives a red dye, which was not isolated but whose soln. dyes wool a brilliant light yellowish red, tannated wool a dull red with faint violet luster and silk a brownish red; the dye soln., treated with satd. NaCl and then dropwise with Na₂CO₃, yields in a short time deep blue-violet flocks, free from halogen and alkali, which in dil. aq. alc. soln. dye tannated wool a delicate blue-violet. *Gallic aldehyde indogenide*, from equal parts of A and indoxyllic acid in alc. and 2 drops concd. HCl heated on the H₂O bath until the evolution of CO₂ ceases, deep dark brown-red cryst. flocks from H₂O, slender leaflets from alc. contg. a few drops of petr. ether, m. 110-5° (decompu.), sol. in alkalies with violet, evanescent color, dyes tannated wool and silk in light yellow-brown to brown-red, silk mordanted with Al₂O₃ in redder shades. With Pd-BaSO₄ or Pt sponge, A absorbs 2 atoms H but the product (E) is a more or less brown amorphous mass often becoming smeary in the air, gives a red color or red ppt. with FeCl₃, has no aldehyde properties but distinctly reduces Fehling soln., reacts vigorously in Me₂CO with CH₃N₃ in Et₂O with formation of an amorphous light yellow powder sol. in NaOH but giving no FeCl₃ test and m. 95-106°; with Ac₂O and C₄H₄N is obtained a yellowish white amorphous powder, m. 183-5°, with 60.23% C, 4.17% H and a mol. wt. of 1820-2010 in boiling Me₂CO. *Gallic aldehyde cyanohydrin*, brownish yellow cryst. warts from Et₂O, decomps. 150-60°, converted by Ac₂O-C₄H₄N into the *tetraacetate*, m. 135°. *Triacetylprotocatechuinaldehyde cyanohydrin*, trapeze-shaped rods from dil. AcOH, m. 112°. C. A. R.

Tannins and similar compounds. X. The tannin of the native oaks. KARL FREUDENBERG AND ERICH VOLBRECHT. *Ber.* 55B, 2420-3(1922); cf. C. A. 17, 86.—The investigation of the tannin of the chestnut (C. A. 16, 356) was discontinued because it was found that the leaves of the oak contain the same new type of tannin in a more readily available form and also because the tannase necessary for the degradation was not, as obtained up to that time, sufficiently powerful. The enzyme has since been investigated and much stronger preps. are now available (C. A. 16, 851), and the study of the new tannin has been resumed, this time on the fresh foliage of *Quercus pedunculata*. A detailed report will appear in the *Ann.*; the present brief paper is published in view of the appearance of the communication of Feist and Schön (C. A. 16, 2385). The *oak-tannin* (A), obtained from a decoction of the fresh leaves through the Pb salt, is freed by vacuum extn. with AcOEt from free ellagic acid (B) and admixed quercetin glucosides. It is accompanied by its own condensation products and cannot be sepd. into different components by fractional vacuum extn. with AcOMe (which slowly exts. it from its aq. soln.) nor by fractional pptn. with Pb(OAc)₂; it is best sepd. from its condensation products by fractional pptn. from alc. with Et₂O. The A is an amorphous red-yellow substance (C 49.9, H 4.2%), easily sol. in H₂O, EtOH and Me₂CO, is strongly acid (titration equiv., about 400), rotates about 35° to the left, contains 23-5% bound B and about 5% bound glucose, the rest of the mol. being an amorphous acid designated *quercussic acid* (C). Warm, very dil. mineral acids split off the glucose before the B, which on further acid hydrolysis is completely split off. The C is therefore combined directly with the B and the glucose is attached to this combination. Dil. alkalies split off, even in the cold, all of the B, which is therefore attached in ester (depside) combination with the C; the glucose is not removed in this process, MeOAc extg. from the B-free hydrolyzate an optically active compound of C, deeply altered by the alkali, with glucose, which is liberated by dil. acids. Acid hydrolysis also decomps. C in great part. Tannase

acts very slowly on **A** but finally effects complete decoumpn., yielding the **C** (**C** 50.2, **H** 3.6%) in amorphous form and having the external properties of the undecompd. **A** but it is optically inactive and cannot be broken down into cleavage products by acids or alkalis. Its titration equiv. is about 400. Since **B** (mol. wt. 302) contains two CO_2H groups titratable in glycerol and is contained in the proportion of 302 parts to about 800 parts (2 equivs.) of **C** in **A** (mol. wt. 1100), which also contains 0.5 mol. glucose (81 parts), **A** must contain $1180/400 = 3 \text{ CO}_2\text{H}$ groups. In the combination of **B** with **C**, therefore, only one of the 4 available CO_2H groups is involved, whence it follows that the 2 equivs. of **C** are contained in the same mol., i. e., that **C** is a dibasic acid with a mol. wt. of about 800, and combines with the dibasic **B** through one of the CO_2H groups; whether this group is one of those in **B** or in **C** has not yet been detd. nor whether the depside is present half free and half as a glucoside or is stoichiometrically combined with the glucose and therefore has a double mol. wt. like **C**. The degradation with tannase is too tedious for purposes of prepn. of **C**, but it has been found that the *Aspergillus niger* which produces the tannase will grow upon the soln. under certain conditions and effect the degradation without changing the **C**. The cupule galls of *Q. pedunculata* also contain **A**, from which **C** can be obtained by subjecting the moist galls to the action of the fungus in a limited supply of air. KOH fusion of **C** has thus far yielded no definite product; no phloroglucinol is formed. C. A. R.

Polyaryl-substituted vinylcarbinols and their derivatives. II. Diarylstyrylcarbinols and their transformation products. KARL ZIEGLER AND CURT OCHS. *Ber.* 55B, 2257-77(1922); cf. *C. A.* 16, 1758; Meyer and Schuster, *C. A.* 16, 3480; Skraup and Freundlich, *C. A.* 16, 3646.—*Di-p-anisylstyrylcarbinol* (**A**), amorphous yellowish powder, and *o*-styrylxanthenol (**B**), m. $158-8^\circ$, have been prepd. by the hydrolysis of the corresponding perchlorates. In the prepn. of **B** there is also formed *di-[o-styrylxanthy] ether* (**C**), m. 172° , which, in fact, becomes the main product when the operation is not carried out with special care. All 3 with HClO_4 in Et_2O regenerate the pure perchlorates. Concd. HCl dissolves **A** with fuchsin-red, **B** and **C** with deep orange-red color; the last soln. after a time deposits a hydrated *o*-styrylxanthy chloride hydrochloride (**D**), $\text{C}_8\text{H}_4\text{O}_4\text{C}_6\text{H}_4\text{C}(\text{CH}_2\text{CHPh})\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$, which can be used instead of the perchlorate

for the isolation of the styrylxantheno derivs. Fuming HBr yields a corresponding compd.; both form with heavy metal halides in halogen acids of AcOH deeply colored ppts. of the corresponding double halides and they also give perhalides. Deeply colored FeCl_3 and SbCl_3 double salts can likewise be obtained from the HCl soln. of **A**. **D** with cold alc. gives first *o*-styrylxanthy ethyl ether (**E**), cubes or prisms from Me_2CO , m. $168-9^\circ$, which, if heated at once with the alc. acid, redissolves with red color and on boiling the soln. deposits the *o*-styrylxantheno (**F**), which can also be obtained by reduction with Me , Pr , *iso*- Pr or *iso*- Bu alcs. or with Zn and AcOH , thus sufficiently proving its constitution although mol. wt. detns. give, probably as the result of association, values 50% higher than the calcd. Unlike **B**, **A** is stable towards boiling alc. acid and it is not reduced with the same ease as **B**, being converted at most into the ether, since the ability of the soln. to form colored salts with acids does not disappear even after long boiling. On the other hand, **A** and **B** behave alike on short boiling with AcOH , yielding smoothly compounds (**G** and **H**) whose comps. agree with those of the allene derivs. $(\text{MeOC}_6\text{H}_4)_2\text{C}:\text{C}:\text{CHPh}$ and $\text{O}(\text{C}_6\text{H}_4)_2\text{C}:\text{C}:\text{CHPh}$, but that they have such a structure is highly improbable, as they do not yield the original perchlorates with HClO_4 under the usual conditions of pptn. Nor are they likely to be indene derivs. formed by rearrangement of the allene compds., as they are dimol. They are probably formed from the allens by polymerization. **H** can also be obtained from **C** or **D** with boiling AcOH or EtCO_2H . On the other hand, the perchlorate of **B** boiled in the same solvent gives a new very stable perchlorate (**I**), which on boiling in alc. smoothly passes into **H**;

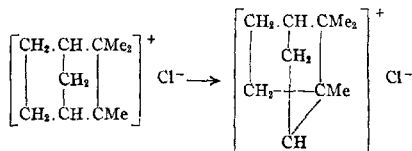
I probably bears to **H** the same relation that the perchlorate of **B** bears to **F**, another fact which cannot be reconciled with the allene structure for **H**. The discovery of **H** explains earlier failures to isolate the radical 9-styrylxanthyl (**J**) by the action of Ag on the chloride; the latter could under no conditions be isolated, as it at once loses HCl and goes over into **H**, probably through the allene compd. It was then attempted to prep. **J** by the action of PhMgBr on the perchlorate of **B**, as it had been found that under such conditions 9-phenylxanthyl perchlorate gives a deep red soln. of phenylxanthyl. **B** perchlorate, however, behaves entirely differently; it reacts vigorously with the Grignard reagent, to be sure, but the soln. retains the faintly yellow color of the PhMgBr, no Ph₂ can be detected and there is obtained a compd. (**K**) having the compn. and mol. wt. of a *o*-phenyl-*o*-styrylxanthene. The Mg compd. of β,β -diphenylvinyl bromide (**L**) with xanthone and (MeOC₆H₄)₂CO gives *o*-[β,β -diphenylvinyl]xanthanol (**M**) and α,α -di-*o*-anisyl- γ,γ -diphenylallyl alcohol (**N**), resp., easily isolated as the perchlorates; **N** is also obtained from Ph₂C:CHCO₂Et and MeOC₆H₄MgBr. The **M** itself has not as yet been isolated; instead there is always obtained the allene deriv. (O), O(C₆H₄)₂C:C:CPh₂, which with acids gives the salts of **M**, and with boiling AcOH rearranges into an isomer no longer forming such salts. Dry HCl in C₆H₆ contg. AcCl converts O into an acid chloride (P), O(C₆H₄)₂C(CH:CPh₂)Cl.HCl, which easily loses 2 mols. HCl with regeneration of O; the normal chloride could not be detected as an intermediate product. The perchlorate of **N** likewise yields 1,1-di-*o*-anisyl-3,3-diphenylallene (Q). With PhMgBr **M** perchlorate behaves entirely differently from **B** perchlorate; there is a violent reaction with formation of an emerald-green Et₂O soln. and deposition of a colorless cryst. compd. (R), which is the analog of C₂Ph₆; it is sol. in cold C₆H₆ with faint yellowish color changing to deep brown on heating and again fading out on cooling; the hot C₆H₆ soln. is completely decolorized by air and on evapn. or treatment with petr. ether yields the peroxide. The green color produced in the Et₂O seems also to be due to a radical, as it disappears on shaking with air. Possibly it has the structure O(C₆H₄)₂-CCH:CPh₂ and the radical corresponding to R the structure O(C₆H₄)₂C:CHCPh₂.

The salts of tetraaryllallyl aces. so resemble those of the diarylstyrylcarbinols, especially in their stability towards hydrolytic agents, that the structure O₄Cl...CR₂CH:CHPh for the latter, rather than the other possible structure, O₄Cl...CHPhCH:CR₂, is made very probable. That the carbinols themselves contain an unchanged styryl group is indicated by the fact that **D** on slow hydrolysis in moist air gives BzH by autooxidation and **A** is oxidized to BzOH; anisilic acid was not isolated but its presence was indicated by the red-violet color reaction with concd. H₂SO₄. That in the action of Grignard reagents on α,β -unsatd. ketones there is only 1,4-addn. (Kohler, *Am. Chem. J.* **31**, 642-61 (1904)) is confirmed by the fact that MeOC₆H₄MgBr and MeOC₆H₄COCH:CHPh (**S**) yield only MeOC₆H₄COCH₂CHPhC₆H₄OMe (**T**) and not a trace of **A**, which, if formed, could have easily been isolated as the perchlorate. **D**, obtained in 5-5.5 g. yield from 5 g. xanthone in 80-100 cc. C₆H₆ slowly added to 18 g. PhCHC:HBz, 2.4 g. Mg and 50-100 cc. Et₂O, boiled 5-10 min., decompd. with cold NH₄Cl, freed from most of the Et₂O *in vacuo* at about 30°, shaken with 40 cc. concd. HCl, sepd. from the C₆H₆ layer and allowed to cryst. in a freezing mixt., small stout red crystals or more or less large leaflets with golden shimmer and red color (by transmitted light), stable for a long time in sealed vessels, quickly weathers in the air (especially moist air) with formation of a colorless substance and evolution of a strong odor of BzH, m. about 95° (decompn.) if plunged into a bath at this temp. but on slow heating it gradually becomes colorless and m. around 170°. The analogous bromide hydrobromide forms stout red crystals. Chloride-zinc chloride double salt, C₂₀H₁₀OCl₂ZnCl₂, long red hydrated needles, darkens 100°, decomp. 188°, from **D** in concd. HCl with ZnCl₂. Ferric chloride salt, from a concd. AcOH soln. of **D** with powdered hydrated FeCl₃, leaflets with golden shimmer and crin-

son color (transmitted light) from AcOH, sinters about 145°, slowly m. 160–80° and then decomps. **H**, short stout prisms from PhMe-benzine, m. 241–2°, mol. wt. in freezing camphor 545. **I**, deep brown-red leaflets, rubs to a pure brown powder, decomps. 248°, deflagrates weakly when heated in a test-tube. **K**, micropisms from AcOH, m. 142–3°, mol. wt. in freezing C_6H_6 322–42. **G**, long stout needles from AcOH, m. 188°, mol. wt. in boiling C_6H_6 660–6, in freezing camphor 688. Meyer and Schuster's "triphenylallene" is also dimol. (found mol. wt., 518–11 in boiling C_6H_6 , 538–42 in freezing camphor). *ms*-Styryldi- β,β' -naphthoxanthyl perchlorate (briefly mentioned in paper I), obtained in 52% yield from dinaphthoxanthone, is, when pure, a quite stable coffee-brown powder with green surface luster, sinters 140°, m. 140–60°, decomps. 174°. *1,3-Di-p-anisyl-3-phenyl-1-propanone* (**T**), m. 89–90°. *2,4,4'-Trimethoxybenzophenone*, from *p*-MeOC₆H₄·COCl and *m*-C₆H₄(OH)₂ by the Friedel-Crafts method, needles from alc., m. 70–1°. *2,2'-Dimethoxybenzohydrol*, from *o*-MeOC₆H₄CHO and *o*-BrC₆H₄OMe by the Grignard method, m. 85–6°, oxidized by CrO₃ to (*o*-MeOC₆H₄)₂CO. *Di-p-anisyl(β,β-diphenylvinyl)methyl perchlorate*, obtained in 50–60% yield from **L** and (MeOC₆H₄)₂CO, cryst. powder with green metallic reflex from a mixt. of CHCl₃ and Et₂O or C₆H₆, deflagrates on rapid heating in a test-tube, m. 130–1° but already softens on long heating on the H₂O bath; heated with C₆H₅N it yields **Q**, m. 102–3°, sol. in concd. H₂SO₄ with violet color. *g-[β,β-diphenylvinyl]xanthyl perchlorate*, obtained in 60% yield from **L**, xanthone and Mg, red needles from PhNO₂-C₆H₆, m. 166° (decompn.). The Et₂O soln. of the crude **M** resulting from its prepn. by the Grignard method gives, when allowed to stand a long time with dil. HCl, *g-[β,β-diphenylvinylidene]xanthene* (**O**), also obtained by hydrolysis of the above perchlorate, m. 205–6°, sol. in concd. H₂SO₄ with bright red color, rearranges on long boiling with AcOH into an *isomer* (best obtained by boiling the perchlorate with AcOH until the initial deep red color has completely disappeared), stout cube-like crystals, m. 173–4°. **P**, deep red needles from CHCl₃-petr. ether contg. AcCl, slowly loses all its HCl in the air or over lime or when treated in PhMe suspension with dry air. *Di-[g-(β,β-diphenylvinyl)xanthyl]* (**R**), obtained in 40% yield, apparently seps. with **1** mol. Et₂O, is somewhat stable in dry solid form in the air. *g-[β,β-Diphenylvinyl]xanthyl peroxide*, dissolves in concd. H₂SO₄ with deep red color. C. A. R.

The equilibrium isomerism between bornyl chloride, isobornyl chloride and camphene hydrochloride. HANS MEERWEIN AND KONRAD VAN EMSYER (WITH JACOB JOUSSEN). *Ber.* 55B, 2500–28(1922).—It was shown recently (*C. A.* 15, 854) that cautious treatment of camphene with HCl gas gives the true HCl addn. product, the tert. camphene-HCl (**A**), m. 125–7°, which is distinguished from its isomers, bornyl chloride (**B**), m. 127–8°, and isobornyl chloride (**C**), m. 161.5°, by the extraordinary mobility of its Cl atom which is quant. eliminated in a short time by H₂O or alc. even in the cold. (Since the true pinene-HCl is now known (see below) it is proposed to reserve the name bornyl chloride exclusively for the compd. m. 127–8° hitherto named pinene-HCl.) The most remarkable property of **A** is that under various conditions, slowly even on mere standing, quickly on heating alone or in contact with acids, it rearranges into the sec. **C**. Certain observations indicated that the rearrangement on heating was never complete but that an equil. was established in the melts or solns. of the 2 isomers similar to that between keto-enol tautomers. To prove the existence of such an equil. isomerism with certainty, a thorough kinetic study has been made of the rearrangement. The necessary method for the quant. detn. of the isomers was based on the fact that **A** is quant. dechlorinated by dil. alc. alkali in 0.5 hr. at room temp. while **C** remains practically unchanged under these conditions. **A** dissociates in soln., even at room temp., into camphene and HCl until an equil. is established; this equil. is dependent on the solvent, the concn. and the temp., and the velocity with which it is established is more-over subject to catalytic influences. Since the rearrangement of **A** and **C** into each other

is catalytically accelerated by HCl, it became necessary to find an exact method for detg. the free HCl in solns. of A. As the decompn. of A by NaOEt proceeds with extraordinary slowness, it was found possible under these conditions to det. the free HCl with the greatest accuracy by using the Et₂O-sol. iodic acid as indicator. The velocity of rearrangement of C at 20° and 40° in 10% solns. in various solvents (5% in MeNO₂, owing to the slight soly. of the A) were made. The velocity differs enormously in different solvents; in cresol it is immeasurably great, in SO₂ isomerization is complete in 10 min. at -15°, in MeNO₂ there is 50% rearrangement in 1.5 hrs. at 20°, in Et₂O there is no change after weeks. The rearrangement is a monomol. reaction; it is therefore a true intramol. shifting of atoms and is not to be ascribed to an alternate splitting off and recombination of HCl, a conclusion fully confirmed by other observations made in the course of the investigation. The velocity consts. tend to diminish with time, especially when the concn. of the A has fallen very low; this is partially due to the dissociation of the A into HCl which, as mentioned above, catalytically accelerates the rearrangement, but that, nevertheless, there is no direct relation between the degree of dissociation and the velocity of rearrangement is shown by the fact that in Et₂O, in which the dissociation is greatest (about 40% in a 10% soln. at 50°), the velocity of rearrangement is least. The velocity of rearrangements in different solvents diminishes in the same order as their dielec. consts. and in the different alcs. it decreases with increase in their mol. wts., *i. e.*, in the same sense as their dielec. consts. diminish, but as A is largely decompd. by alcs. until equil. is reached, the results obtained with them cannot be compared directly with those obtained with other solvents. These results can be explained only on the assumption that the rearrangement of A is preceded by its ionization and therefore really consists, not in a migration of the Cl atom, but in a regrouping of the cation:



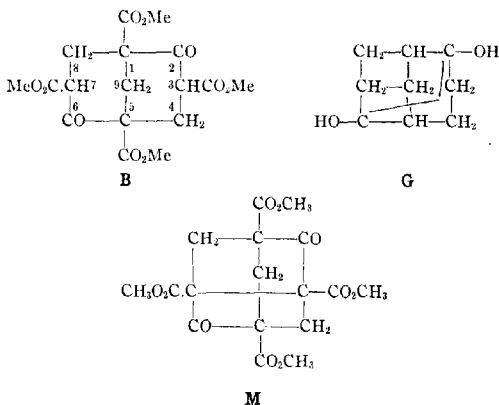
There is, however, no complete parallelism between the velocity of rearrangement of the A and the dielec. const. of the solvents in which it occurs; in cresol, SO₂ and PhOMe, especially, the rearrangement is far more rapid than would be expected from their dielec. consts. and in Et₂O it is slower. Of these solvents, cresol and SO₂ are conspicuous, from work with Ph₃CCl, for their ability to form intensely colored complexes, and Et₂O for the opposite property (of decolorizing the colored solns. of Ph₃CCl), and the work of Schlenk and Pfeiffer on quinhydrone formation has shown that phenol ethers are qual. to be grouped with phenols as regards their ability to form complexes. It may therefore be assumed that A, just like Ph₃CCl, forms complexes with PhOH and SO₂ and, to a lesser degree, with PhOMe and that these complexes increase the mobility of the Cl atom or the ionization of the A. The influence of this complex formation can be clearly shown by the catalytic influences to which the rearrangement reaction is subject. All those compds. which form double compds. with Ph₃CCl catalyze the reaction (the halogen acids and, in order of decreasing influence, anhyd. SbCl₅, SnCl₄, FeCl₃, HgCl₂, SbCl₃, PCl₃ and SiCl₄ are without influence); in the presence of 0.001 mol. SbCl₅ or SnCl₄ per l. the rearrangement of A is complete in 5 min. The reaction is also monomol. in the presence of these catalysts, and in fact the consts. are in general somewhat better than without catalysts, as the disturbing influence of the HCl set free by dissociation is to a certain extent overcome by the catalyst. The influence of the

the catalyst is dependent upon the medium; *e. g.*, in Et_2O 0.2 *N* HCl has practically no influence. The influence of the solvent on the degree of ionization of **A** should also manifest itself in other reactions of **A** which may be considered as being ionic, such as the action of MeOH on **A**, which, as will be shown later, results first in the formation of the Me ether of camphene hydrate, a direct counterpart of the transformation of Ph_2CCl into Ph_2COMe . As a matter of fact, the influence of solvents on the velocities of this reaction and on those of the rearrangement of **A** into **C** are entirely similar. To test whether the enormous slowing action of Et_2O might be due to the formation of an oxonium salt, the influence of $\text{C}_6\text{H}_5\text{N}$ was detd.; it was found to slow up the reaction very greatly, to be sure, but not as much as Et_2O , the reason for whose specific action remains unexplained. Expts. on the influence of various solvents on the velocity of alcoholysis of Ph_2CCl by AmOH gave results entirely analogous to those obtained with **A** and MeOH. The % of **A** at equil. in various solvents and at various temps. are as follows: PhNO_2 : 50°, 1.62; 70°, 3.92; 125°, 13.10. PhCl : 50°, 0.58; 70°, 1.31; 125°, 10.00. PhBr : 125°, 8.37. PhOMe , 125°, 10.83. Cymene, 125°, 4.37. According to the LeChatelier law, then, since increase in temp. favors **A** its rearrangement into **C** is exothermic. While the velocity of the reverse rearrangement of **C** into **A** cannot be measured, it can easily be shown that it is subject to the same catalytic influences as the rearrangement of **A** into **C**; it is merely necessary to measure the velocity of decompn. of **C** into camphene or camphene hydrate and HCl, as this decompn. is preceded by a rearrangement into **A**. H_2O contg. PhOH decomps. **C** 100 times faster than alc. KOH, and the decompn. by H_2O alone is considerably more rapid than that by alc. KOH, thus showing the strong catalytic influence of acid. The same relationships as the above hold for the rearrangement of **C** into **B** which, however, takes place with much greater difficulty than that of **C** into **A**, owing to the small ionization of **C** and the practically complete non-ionization of **B**, as shown by the behavior of the 3 substances towards MeOH; **A** is almost instantly converted, even in the cold, into camphene hydrate Me ether and **C** in 14 days at 30° into isobornyl Me ether, while **B** does not appreciably react with boiling MeOH. In the absence of catalysts and in non-dissociating solvents **C** rearranges into **B** with extreme slowness even at 130°, while in cresol and liquid SO_2 and in PhCl in the presence of SnCl_4 (the conditions found to be most favorable) the velocity of rearrangement is already considerable at 70°. In these expts. the position of the equil. was not detd.; at 100° it still lies almost completely on the side of **B**; in PhCl at 130° there was about 3% **C** after 32 days. The true pinene-HCl (cf. Aschan, *C. A.* 16, 2324) has been obtained in cryst. form, although not quite free from **B**, by passing HCl into pure pinene in petr. ether at -60°; it is instantly decompd. by H_2O and alc., titrates in alc. like free HCl, can, like **A**, be so stabilized by Et_2O that the free HCl resulting from its dissociation can be titrated; after addn. of 0.5 part (by wt.) of Et_2O , about 50% of the HCl passed into the pinene remains uncombined after 24 hrs., with 0.07 part Et_2O about 16% remains uncombined, while in the absence of Et_2O or in the presence of petr. ether combination is practically complete. As **A** worked in the presence of Et_2O , the regeneration of pinene (max. yield, 24%) observed by him on heating with PhNH_2 does not seem established with certainty. The **A** (best preps., 93.3% pure) was prepd. from pure camphene in Et_2O with HCl gas, the **C** (99.6% pure) in 138 g. yield from 300 g. camphene in 150 g. EtBr satd. with HCl at 10-20°, heated 6 days uninterruptedly at 55° under a reflux, freed from most of the EtBr with air, dried *in vacuo* over KOH and recrystd. from 220 g. AmOH. Below are the velocity consts. (time in hrs.) for the rearrangement of **A** into **C**: At 20°: MeNO_2 0.378, MeCN 0.1260, PhNO_2 0.0397, PhCN 0.0396. At 40°: PhOMe 0.0247, PhBr 0.0184, EtBr 0.0149, PhCl 0.0123, C_6H_5 0.00396. At 42°: petr. ether 0.00617.

C. A. ROUITLER

Bicyclic and polycyclic compounds with bridging atoms. II. Bicyclo-1,3,3-

nonane and derivatives. HANS MEERWEIN, FRANZ KIEL, GUSTAV KLÖSCHEN AND EDWIN SCHOCH. *J. prakt. Chem.* **104**, 161-206(1922); cf. *C. A.* **7**, 3475; **13**, 2661.—When bicyclo-[1,3,3]-nonane (A) is depicted in 3 dimensions it is seen that this arrangement gives no strain in the bonds connecting the 9 C atoms; this accounts for the stability and ready formation of these compds.; it is also likely that such compds. occur naturally; the geometrical arrangement of the C atoms is identical with the cryst. structure assigned to the diamond by Laue and Bragg. The derivs. of A show a marked resemblance to the corresponding camphor derivs. in phys. and chem. but not in physiol. properties. *Methyl bicyclo-[1,3,3]-nonane-2,6-dione-1,3,5,7-tetracarboxylate* (B) was prepd. as previously reported from a mixt. of 1 mol. $\text{CH}_2[\text{CH}(\text{CO}_2\text{Me})_2]_2$, 2 mols. $\text{CH}_2:\text{C}(\text{CO}_2\text{Me})_2$ and NaOMe; best results were obtained by continuing the boiling at least 8 hrs. until the mixt. solidifies from the formation of the Na salt; a 66% yield was obtained. B was hydrolyzed to the di-Me ester and the latter when heated for 1 hr. in an autoclave to 220°



with 2 parts H_2O gives *bicyclo-[1,3,3]-nonane-2,6-dione* (C) which was purified by distn. *in vacuo*. *Diacetylbicyclo-[1,3,3]-nona-2,6-diene-2,6-diol* (D), prepd. by heating 5 g. C, 30 g. Ac_2O and a drop of H_2SO_4 for 2 hrs. at 145°, cooling, decomp. the excess Ac_2O with H_2O , washing the sepd. oil with Na_2CO_3 and drying, gave needles from petr. ether, m. 78-9°; D in CCl_4 decolorizes Br_2 with evolution of HBr ; reduction of D with H and Pt yields A, acetylbicyclo-2-nonanol and diacetylbicyclononane-2,6-diol. C gives a *disemicarbazone* (E) forming a white powder from AcOH , m. 226°, very slightly sol. in all solvents. A was prepd. by heating 5 g. E and 5 g. Na in 50 cc. abs. EtOH to 220° for 6 hrs. (cf. *C. A.* **7**, 790), steam distg. and recrystg. the distillate from $\text{EtOH}-\text{H}_2\text{O}$; A, best obtained by extg. the steam distillate with Et_2O , washing the ext. with H_2O , drying over CaCl_2 , evapg. the Et_2O , heating the residue 2 hrs. with Na and distg., b. 168.5-70° (yield 40%), forms a white, plastic mass resembling camphane in appearance and odor, readily sublimed, crystals from AcOH or MeOH , m. 145-6°; A does not decolorize Br in CCl_4 . *trans-Bicyclo-[1,3,3]-nonane-2,6-diol* (F) was prepd. by passing CO_2 through a well stirred soln. of 60 g. C in 1750 cc. H_2O at 20-5° and adding 3.5% Na-Hg in 50-g. portions until test portions and AcOH no longer ppt. with PhN_2H_3 ; the soln. is decanted from Hg, acidified with H_2SO_4 , made slightly alk. with Na_2CO_3 and evapg. *in vacuo*; the dry residue was extd. in a Soxhlet with CHCl_3 and the ext. evapg. to dryness; this is a mixt. (H) of equal parts F and *tricyclo-[1,3,3,3,0]-*

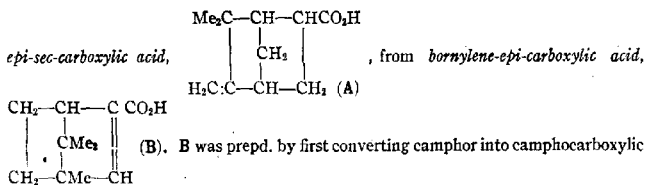
nonane-2,6-diol (G) which is fractionally recrystd. from MeOH or EtOAc, when **F** seps. from in octahedrons and then **G** in needles; **F** from MeOH or EtOAc m. 219°, is readily sol. in H₂O, EtOH, CHCl₃, EtOAc or Me₂CO and insol. in PhH or CCl₄; when H₂SO₄ is added to **F** in EtOH or in Ac₂O a red color is obtained (cf. v. Baeyer, *Ber.* **25**, 1840 (1892); Wallach, *Ann.* **239**, 27 (1887); Liebermann, *Ber.* **18**, 1804 (1885)); the *diacetyl derivative* of **F** m. 35°, b₁₇ 173–4°; *dibenzoyl derivative*, prepd. in a cold C₆H₅N soln., forms leaves from EtOH, m. 96–7°; **F** oxidized in AcOH with CrO₃ gives **C**. *Bicyclo-[1,3,3]-nonene-6-ol-2* (**I**) was prepd. by dissolving 25 g. **H** in 100 cc. 23% H₂SO₄ and warming to 145° after 40 cc. H₂O have distd. and the concn. of the H₂SO₄ is 38%. **I** begins to distil with steam; H₂O is added slowly to keep the concn. of H₂SO₄ at 38%; **I** resembles camphor in appearance and odor, is readily sol. in org. solvents, m. 133°, b. 224–6°; air slowly oxidizes **I** to a yellow oil; the *acetyl derivative* of **I** is a colorless oil, b₁₂ 111–2°; reduction of **I** in AcOH with Pt black and H at 40°, filtering and adding H₂O to the filtrate ppts. in 40% yield *bicyclo-[1,3,3]-nonan-2-ol* (**J**), which is purified by washing the Et₂O soln. with Na₂CO₃, drying over K₂CO₃ and subliming; it is readily sol. in org. solvents, resembles isoborneol in odor, m. 185°, *acetyl derivative* of **J**, b₂₀ 128°. An 83.5% yield of *bicyclo-[1,3,3]-nonan-2-one* (**K**) was obtained by oxidation of 8.5 g. **J** with 6.8 g. K₂Cr₂O₇, 5.8 g. concd. H₂SO₄ and 34.8 g. H₂O at 85–90° for 30 min., diln. with H₂O and steam distn.; purified by decompn. of its *semicarbazone* (**L**) with 15% H₂C₂O₄ it has a camphor odor and m. 150°. **L** from EtOH, m. 180–1°, BzH and PhCH:CHCHO with NaOEt yield the *3-benzylidene*, m. 127–80°, and the *3-cinnamylidene*, m. 116–7°, *derivatives*, resp. **G** may be sepd. from **H** but is best prepd. by adding BaCO₃ to the acid residue in the prepn. of **I**, filtering while hot, washing the ppt. repeatedly with hot H₂O, evapg. the filtrate to dryness *in vacuo*; crystals from EtOAc or EtOH, m. 141°, sol. in CH₃, slightly sol. in Et₂O, PhH, PhMe or CCl₄ and volatile in steam; CrO₃ in AcOH oxidizes **I** to **C**; a *diacetyl derivative* of **I** from dil. EtOH, m. 121°; *dibenzoyl derivative*, prepd. in C₆H₅N, forms crystals from EtOH, m. 153–4°; *diphenylurethan derivative*, from CHCl₃, m. 201°. *Methyl tricyclo-[1,3,3,3',o']-nonane-2,6-dione-1,3,5,7-tetracarboxylate* (**M**) was prepd. by adding 50 g. **B** to 3 g. Na in 100 cc. abs. MeOH, adding slowly with stirring 21 g. Br₂ in 50 cc. MeOH, then just sufficient Na in MeOH to make slightly alk. to phenolphthalein; **M** ppts. and is recrystd. from xylene or AcOH, m. 247–8°, readily sol. in CHCl₃ or PhH, slightly sol. in AmOH and insol. in EtOH or Me₂CO. **B** treated with a 3% soln. of 1 atom Na in MeOH yields a *monosodium salt* (**N**); similarly 2 atoms Na gives a *disodium salt* (**O**). *Methyl 3-bromotricyclo-[1,3,3,3']-nonane-2,6-dione-1,3,5,7-tetracarboxylate*, obtained by treatment of **N** with Br₂ in MeOH forms rhombs from MeOH, m. 154°; similarly **O** gives the *3,7-dibromo derivative* from EtOH or xylene, m. 142° (decompn.). Na in MeOH after 0.5 hr. converts **M** quant. into *methyl cycloheptane-1,1,3,3',5,6* (or *1,3,5,5,6,6* or *1,1,3,5,6,6*)-*hexacarboxylate* (**P**) which is readily sol. in CHCl₃ or Me₂CO, slightly sol. in AcOH, AmOH, MeOH or EtOH, m. 128°. Hydrolysis of **P** with Ba(OH)₂ for 3 hrs. at 105°, pptg. Ba²⁺ with H₂SO₄, filtering and evapg. *in vacuo* at 40° gave *cycloheptanhexacarboxylic acid* (**Q**) with 2 H₂O; the anhydrous acid forms crystals from AcOH or HCO₂H, m. 177° (decompn.) and is sol. in H₂O, EtOH or MeOH. **Q** on heating with H₂O and a trace of HCl until CO₂ evolution ceases, evapg. to dryness and recrystg. from AcOH or HCO₂H gave *cycloheptane-1,3,5,6-tetracarboxylic acid* (**R**), m. 233°, which is readily sol. in H₂O, MeOH, EtOH and slightly sol. in Me₂CO; heating above 233° or boiling with AcCl and recrystg. from Ac₂O gives the *dianhydride* of **R**, m. 197–8°, which is readily sol. in Me₂CO or CHCl₃, slightly sol. in AcOH or HCO₂H and insol. in H₂O or NaOH. **M** heated with Ba(OH)₂ soln. for 7 hrs. at 105°, freed from Ba with H₂SO₄, filtered, evapg. and recrystd. from HCO₂H gave *bicyclo-[1,2,3]-octanone-8-pentacarboxylic acid* (?), m. 184–5° (decompn.), which is readily sol. in H₂O, EtOH or AcOH and slightly sol. in

Me_2CO or EtOAc ; 2.5 mols. CO_2 are lost on heating to 240° . *Bicyclo-[1,3,3]-nonene-6-one-2* (S) was prepd. by treating I with CrO_3 in 50% AcOH at $20-5^\circ$. steam distg., extg. the distillate with Et_2O , washing the ext. with H_2O and Na_2CO_3 , drying with CaCl_2 , evapg. the Et_2O , treating in dil. EtOH with $\text{NH}_2\text{CON}_2\text{H}_4\cdot\text{HCl}$ and NaOAc and recrystg. the *semicarbazone* (T) from MeOH , m. $190.5-1^\circ$; T with 10% H_2SO_4 gave S, m. 82° , b. $213-17^\circ$, decolorizes KMnO_4 in Me_2CO and also Br_2 in CCl_4 , oxidized by air and has a camphor odor; the *cinnamylidene derivative* forms yellow needles from EtOH , m. 117° . *trans-2,6-Diaminobicyclo-[1,3,3]-nonane* (U), prepd. by reducing the dioxime of C in EtOH with Na, raising the temp. to 150° , then distg. with superheated steam at $160-70^\circ$, collecting U in HCl , and evapg. the acid solu. gives a *dihydrochloride* (V) from which by distn. *in vacuo* with solid NaOH U is obtained as a colorless oil, b₂₈ $140-7^\circ$; purified by distn. *in vacuo* with solid Ba(OH)_2 it forms colorless, hygroscopic crystals, b₁₄ $125-30^\circ$; a *diacetyl derivative* of U, from EtOAc or Ac_2O , m. 214° ; a *dibenzoyl derivative* from AcOH , m. 351° (cor.). *2-Aminobicyclo-[1,3,3]-nonene-6*, prepd. by subliming V, dissolving in NaOH , steam distg., collecting the distillate in HCl , evapg. to dryness, distg. with solid NaOH *in vacuo*, dissolving the distillate in Et_2O , drying over NaOH and redistg. over solid Ba(OH)_2 *in vacuo*, m. 37.5° , b₁₇ 104° , has a nicotine odor, is slightly sol. in H_2O and is oxidized by air.

N. A. LANGE

Preparation of bornylene. HANS MBERWIN and JACOB JOUSSEN. *Ber.* 55B, 2529-33(1922); cf. preceding abstr.—By the methods hitherto known, the splitting off of HCl from bornyl chloride (A) results in the formation, not of bornylene (B), but of its rearrangement product, camphene (C), because the normal splitting off of HCl requires a very high temp. (about 230°) so that the rearrangement of A into isobornyl chloride (D) and C.HCl (E) described in the preceding abstr. occurs before the HCl is eliminated. In order to be able to obtain B from A it is necessary, therefore, to know under what conditions this rearrangement of A occurs not at all or only very slowly, and as it is similar to and subject to the same catalytic influences as the rearrangement of D into E, it is simpler, experimentally, to det. the desired conditions by a study of the latter rearrangement. Accordingly the decompn. velocity or, what amounts to the same thing, as shown in the preceding abstr., the rearrangement velocity of D on treatment with alcoholates under different conditions was studied. The velocity of rearrangement diminishes with increasing concn. of the alkali, with decreasing amts. of H_2O and with increasing mol. wt. of the alc. These 3 facts can be explained on the assumption that the rearrangement is favored, in a way which is not yet clear, by OH ions. These observations made on D hold equally well for A; the content of B in the product of decompn. increases with increasing alkali concn., decreasing H_2O content and increasing mol. wt. of the alc.; by heating 30 g. A with 10 g. K in 100 cc. AmOH 6 hrs. in sealed tubes at 230° , there was obtained 19 g. of a product b. $146-8^\circ$, m. $108-7^\circ$, contg. 93% B. The elimination of HBr from bornyl bromide with K in AmOH occurs almost instantaneously at about 190° so that the operation can be carried out in an open vessel and the resulting B is as pure as that obtained from A. C. A. R.

Camphene-*epi*-*sec*-carboxylic acid. J. BRÄGER. *J. prakt. Chem.* 104, 1-27(1922).—In continuation of earlier work in the same field (C. A. 6, 991) B. has prepd. *camphene-*



acid by a modification of the Brühl method (cf. *Ber.* 36, 1305(1903)) and then reducing this acid electrolytically by Bredt's method to borneol-*o*-carboxylic acid, which by dehydration gives the desired bornylene deriv. B with fuming aq. HBr gives the tertiary hydrobromide (C) of A, m. 157°, which with alkali gives the tertiary HO-acid (D), m. 176°. Boiling the latter with water gives A, m. 76°. C can be converted into A directly by fusion with 5 parts quinoline. A is easily sol. in most org. solvents, b_{14} 157°, b 114°. With aq. HBr it reforms C. The NH_4 and Ag salts were prepd. The anhydride of A, b_{14} 205°, was prepd. by boiling D with 5 mols. Ac_2O . The Et camphene-*epi*-*sec*-carboxylate was prepd. from the Ag salt of A and EtI. The ester is weakly optically active, $[\alpha]_D^{25} + 4.04^\circ$, has a pleasant odor, b_{22} 128°, $d_4^{17.5}$ 0.9888, n_D 1.47551. A gave with $\text{Hg}(\text{OAc})_2$ an addn. product, confirming the presence of the $=\text{CH}_2$ grouping (Balbiano's reaction; cf. *Ber.* 36, 3575(1903); *C. A.* 3, 2156). Oxidation of A with alk. KMnO_4 gave in 6% yield the tribasic carboxycamphenecamphoric acid, $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{H})\text{CH}_2\text{CHCMe}_2\text{CO}_2\text{H}$ m. 234–6° (decompn.). Acetylation of A

according to Bertran-Walbaum method gave a mixt. of two acetates, which could be sep'd. in ligroin into *acetylborneol-p*-carboxylic acid (E), m. 150°, and *acetylisoborneol-o*-carboxylic acid (F), m. 116°. The former was hydrolyzed to *p*-borneolcarboxylic acid, m. 181°, and this oxidized with KMnO_4 to *p*-camphocarboxylic acid, m. 133°; the latter was hydrolyzed to *isoborneol-o*-carboxylic acid, m. 172°, which could not be oxidized by KMnO_4 but with Ac_2O , followed by alc. KOH it gave B, m. 111°, and with HNO_3 camphoric acid, m. 203°. Rapid heating of E gave a lactone, while F gave similarly B. Finally a system of nomenclature for the whole camphane series is proposed. O. B. H.

Reactions between azobenzene hydrochloride and aromatic hydrocarbons. II. RUDOLF PUMMERER, JOSEF BINAPFEL, KARL BITTNER AND KARL SCHUEGRAF. *Ber.* 55B, 3095–104(1922); cf. *C. A.* 16, 1403.—PhMe reacts with $(\text{PhN})_2\text{HCl}$ in the presence of AlCl_3 even more readily than does C_6H_6 ; the product is $\text{MeC}_6\text{H}_4\text{C}_6\text{H}_4\text{NHNH}_2$ (Kligel and Huber, *C. A.* 15, 843). The yield varies between 35% and 50% as compared with 16% obtained by K. and H. 3-Methyl-4-aminobiphenyl, b_{14} 190–1°, is obtained in 35% yields by the reaction of (*o*- $\text{MeC}_6\text{H}_4\text{N}$) $_2$ and C_6H_6 with 2.5 equivs. of AlCl_3 at 20–30°. Hydrochloride; the aq. soln. gives an intense green color with FeCl_3 . Acetate, m. 165.5°. Benzylidene derivative, yellow leaflets, m. 108.5°. In the prepn. of *p*-naphthylaniline special care must be taken to have the $(\text{PhN})_2$ and C_6H_6 very pure and dry. The HCl salt is transformed into the benzylidene derivative, yellow, m. 164.5°, and this saponified by dil. HCl to the free base, leaflets, m. 94–5°. *p*-Amino-1,4-diphenylbenzene, from $(\text{PhN})_2$ and Ph_2 , glistening Ag-white leaflets, m. 198°. This yields a yellow solid diazonium salt, which couples with R-salt to form a bluish red dye. Upon decompn. of the sulfate with NaSnO_2 , 1,4- $\text{C}_6\text{H}_4\text{Ph}_2$ results, thus establishing the constitution of the NH_2 deriv. C. J. WEST

The addition of benzene to quinone. RUDOLF PUMMERER AND ERNST PRELL. *Ber.* 55B, 3195–16(1922); cf. preceding abstr.—In view of the peculiar reaction of $(\text{PhN})_2$ with C_6H_6 it was of interest to det. whether quinone is capable of the same reaction. This is the case; when $\text{C}_6\text{H}_6\text{O}_2$ and AlCl_3 are brought together in C_6H_6 , the intense blue color of the double salt is quickly observed. The addn. product is diphenylquinhydrone, which may be oxidized to the known $\text{Ph}_2\text{C}_6\text{H}_4\text{O}_2$. Since *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ is isolated from the mother-liquors the reaction probably proceeds as follows: $3\text{C}_6\text{H}_6\text{O}_2 + 2\text{C}_6\text{H}_6 = \text{diphenylquinone} + 2\text{C}_6\text{H}_4(\text{OH})_2$. 2,5-Di-*p*-tolylhydroquinone (A), greenish white 6-sided plates, m. 189°, was obtained by the action of 0.5 mol. $\text{C}_6\text{H}_6\text{O}_2$ and 0.5 mol. AlCl_3 in excess of PhMe at 0°. Diacetate, needles, m. 204°. Oxidation of an alk. soln. of A with air gave 2,5-di-*p*-tolylquinone (B), citron-yellow leaflets, m. 220°; from AcOEt B crysts. in orange-red compact bipyramidal forms (monoclinic prismatic),

$a : b : c = 1.3035 : 1 : 1.7328$; β $129^\circ 14.5'$; $m(110)$, $w(11\bar{1})$. The red form is obtained from the yellow by heating the dry solid on the H_2O bath and is stable in the dark for many weeks, but in the light becomes covered with a thin layer of the yellow form. If the above reaction is carried out in CS_2 and a moderate stream of HCl passed through the mixt. during the entire time (5 hrs.) there is obtained from 21 g. $C_6H_4O_2$ 2.7 g. **B** and about 5 g. of the quinhydrone of **B**. *p,p'*-Dihydroxy-2,5-diphenylquinone, by the reaction of 0.1 mol. $C_6H_4O_2$, 0.3 mol. $AlCl_3$ and 0.25 mol. $PhOH$ in CS_2 and treating the dark reaction product suspended in $AcOH$ with an excess of $FeCl_3$, brownish red needles, sinters 287° , m. above 327° . The concd. H_2SO_4 soln. is green, the alk. soln. intensely violet, changing to brown. Diacetate, small, felted prisms, m. 260° (decompn.). The hydroquinol forms glistening leaflets, or small needles, m. 303° . Tetraacetate, m. 250° . *p,p'*-Dimethoxy-2,5-diphenylquinone, orange-red needles, m. 231° . Hydroquinol, grayish white leaflets, m. 203° .
C. J. WEST

Biphenyleneethylenes. HEINRICH WIELAND, FRITZ REINDL and JUAN FERRER. *Ber.* 55B, 3313-7(1922); cf. Sieglitz and Jassoy, *C. A.* 17, 386.—The method of Manchot and Krische (*Ann.* 337, 170(1904)) for making biphenyleneethylenes (9-methylenefluorene) (**A**), gives really no **A**, but chiefly a mixt. of fluorene and diphenyleneethylenes. **A** was made by heating 9-methylfluorene (in 2-g. portions) with $AlPO_4$ *in vacuo*; it was rapidly converted by heat or light to a polymer (**B**) $(C_{14}H_{10})_n$, amorphous powder, softens 270° , with some reformation of **A**. By heating the **B**, further quantities of **A** were obtained, and all the crude **A** was converted by Br_2 to δ,g -dibromo-9-methylfluorene (**C**), broad needles, m. 143° (decompn.). **C**, in 0.2-g. portions, is debrominated with Zn dust and $AcOH$ in alc., and recrystd. from Et_2O . If all steps are carried out in artificial light, **A** is obtained, m. 53° , and stable for some hrs. if not too strongly illuminated. In Et_2O it is somewhat more stable. It is suggested that **B** may be tribiphenylenecyclohexane.
BEN. H. NICOLET

The semipinacol rearrangement of the alkylhydrobenzoins; influence of the alkyl radical. M. TIFFENEAU and A. ORÉKHOFF. *Compt. rend.* 175, 964-7(1922).—The alkylhydrobenzoins, treated with acids, undergo the hydrobenzoin rearrangement: [1] With concd. H_2SO_4 they are dehydrated, yielding, in part, alkyldeoxybenzoin; [2] without rearrangement, and, depending on the alkyl radical, varying quantities of diphenylalkylketone; [3], by a semipinacol rearrangement. Reaction 2 resembles 1 in that the tertiary OH is eliminated, while in 3 the O of the tertiary OH persists. The expts. of T. and O. (cf. *C. A.* 15, 3477), wherein butylhydrobenzoin on dehydration, yields 2 and 3 while isobutylhydrobenzoin yields only 2 proves that the stability of the tertiary OH is not a function of the mol. wt. of the substituent alkyl radical. New expts., not reported in detail, confirm the conclusion that radicals having, in the notation of Meerwein, a strong capacity of satn. (e. g., Me, iso-Bu, Ph), form hydrobenzoins which dehydrate, yielding only 2, while those which have a weak or intermediary capacity (iso-Pr, cyclohexyl, Et, Pr, Bu, iso-Am), yield 2 and 3. These cases in which the sec. OH becomes less stable than the tertiary seem to verify the hypothesis that the H_2SO_4 is added to the OH and modifies the distribution of affinity.
I. P. ROLF

Free radicals. P. WALDEN. *Rec. trav. chim.* 41, 530-56(1922).—This paper reviews the history of free radicals from the time of Lavoisier. After 1850 with the development of the theory of the tetravalence of C and the periodic law chemists thought less of isolating free radicals but generally used the conception symbolically in interpreting reactions of org. compds. Williamson's work on mixed ethers, Butlerov's CH_2 , Laar's tautomerism and Nef's methylene dissoc. involved the actual existence of free radicals. In 1900 the 1st actual free radical, Ph_3C , was isolated by Gomberg. Developments in the study of a few dozen other examples discovered since that date are too fully

reviewed to be briefly abstracted. An abstr. of W.'s follows: Modern research has finally decisively answered a 100-year old problem by replacing the metaphysical conception of radicals (org.) by physically free radicals. In free radicals synthetic chemistry has acquired a unique and highly reactive type of chem. compd. which is to be compared to the free elementary atom. These radicals have brought new problems into theoretical chemistry concerning the no., manner of action and the nature of valences. General phys. chemistry has a new type of materials especially for stoichiometry and the investigation of phys. properties and their relation to chem. constitution. These free radicals and their halides or metallic derivs. supply a new type of "salts" for comprehensive electrochem. investigation. The nature of the solvent is of peculiar importance in these investigations and the question of solvate formation has in these cases a peculiar theoretical and practical importance. In general this new field of free radicals is now fruitful ground for investigation by all depts. of chemistry. For the large amt. of bibliographic material see the original.

E. J. WITZEMANN

The question of the course of organic reactions. HEINRICH WIELAND. *Rec. trav. chim.* **41**, 576-9(1922).—All transformations of org. compds. that take place between 2 components doubtless do so by way of a mutual addn. This mechanism rules in the entire realm of unsatd. reaction systems and largely leads directly to the end products. The relations are less simple with the satd. compds. (e. g., $\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{MeCl} + \text{HCl}$). The 2 mols., although represented as satd., are surrounded by an energy field into which the 2 mols. enter, resp., when they collide and in which the transformation takes place with the loss of energy. In terms of this view intramol. rearrangements take place without any change of position of the groups and without the intervention of free radicals. These changes all occur within the sphere of the mol. energies. In the case of malonic acid (A), which gives $\text{AcOH} + \text{CO}_2$ on heating, W. concludes that A does not dissociate into $\text{CH}_2\text{CO}_2\text{H} + \text{CO}_2 + \text{H}$ and that $\text{CH}_2\text{CO}_2\text{H}$ and H combine, but rather that CO_2 is expelled from the mol. sphere without the formation of any free H_2 , since none could be detected. Similarly $\text{Ph}_3\text{CN}:\text{NCPh}_3$ decomps., giving $2\text{Ph}_3\text{C} + \text{N}_2$. In the case of $\text{PhN}:\text{NCPh}_3$ 30% of the calcd. amt. of Ph_3C was isolated as the peroxide on decompn. in an indifferent solvent. The N_2 was completely removed from the mol. so that the decompn. of this azo compd. (unlike that of A above) involves the appearance of free radicals (Ph_3C and C_6H_5). The C_6H_5 radical does not polymerize to give Ph.Ph but C_6H_6 instead. This is contrary to the usually expected result. The source of the H is unknown. This means that all transformations in which radicals may take part must be studied in detail. Other instances are briefly mentioned.

E. J. WITZEMANN

Nature of the carbon union. Free pentaphenylethyl. W. SCHLENK AND HERMANN MARK. *Ber.* **55B**, 2285-99(1922).—Attempts to prep. *pentaphenylethyl* (A) by the action of metals on $\text{Ph}_2\text{CCPh}_2\text{Cl}$ failed owing to the impossibility of prepg. the chloride by replacing the HO group of $\text{Ph}_2\text{CCPh}_2\text{OH}$ with Cl. When, however, Ph_2CNa in Et_2O (protected from air, moisture and CO_2) is treated dropwise with Ph_2CCl_2 in Et_2O the intense yellow-red color of the Ph_2CNa soln. at once becomes lighter and there results a permanent light red color, corresponding in intensity to that of a moderately concd. Ph_3C soln. and in its shade and spectrum, differing completely from that of a Ph_2CNa soln. On shaking with air the soln. immediately loses its color and afterwards quickly assumes the yellow color of Ph_3C solns. and now shows the typical behavior of the latter (repeated decolorization by shaking with air with subsequent return of the color on standing until finally the decolorization is permanent, and deposition of $(\text{CPh})_2\text{O}_2$). No $\text{Ph}_2\text{C}:\text{CPh}_2$, which is difficultly sol. in Et_2O , could be detected (only NaCl sepd. during the reaction), so that the Ph_2C could not have been formed (or at least to only a very small extent) according to the equation $4\text{Ph}_2\text{CNa} + 2\text{Ph}_2\text{CCl}_2 = \text{Ph}_2\text{C}:\text{CPh}_2 +$

$4\text{Ph}_3\text{C} + 4\text{NaCl}$, and it must have been formed according to the scheme $2\text{Ph}_3\text{CNa} + \text{Ph}_2\text{CCl}_2 \longrightarrow 2\text{NaCl} + \text{Ph}_2\text{CCPh}_2\text{CPh}_2 \longrightarrow \text{Ph}_2\text{CCPh}_2 + \text{Ph}_3\text{C}$. On filtering the red reaction mixt. from the NaCl in N, concg. at a low temp. and cooling in a freezing mixt., there sep. after a long time, together with very small light yellow crystals of C_6Ph_6 , larger brown-red scales of A, mol. wt. in freezing C_6H_6 418. $\text{Ph}_3\text{CNaCNaPh}_3$ and Ph_3CCl react chiefly to form NaCl, $\text{Ph}_2\text{C}:\text{CPh}_2$ and PhC_3 , but also to some extent to form $\text{Ph}_3\text{CPh}_2\text{CPh}_2\text{CPh}_2 \longrightarrow 2\text{A}$, the presence of the A being shown by treating the red soln. of the reaction product with Cl in CHCl_3 to disappearance of the red color (formation of $\text{Ph}_2\text{CCPh}_2\text{Cl}$) and then with H_2O , whereupon $\text{Ph}_2\text{CCPh}_2\text{OH}$ sepd. The identity of A was established not only by analysis and mol. wt. detns. but by the following reactions: It takes up Cl eagerly with formation of *pentaphenylchloroethane*, which is hydrolyzed by moisture with extraordinary ease to $\text{Ph}_2\text{CCPh}_2\text{OH}$ and regenerates A with Cu bronze in Et_2O ; with Na-Hg it gives a dark brown *sodium derivative* behaving in all respects like Ph_3CNa and immediately converted by H_2O into *pentaphenylethane*, crystals from AcOH , m. 173° , turning yellow (in a sealed tube under CO_2 it m. 176°). Solns. of A shaken with air are permanently decolorized, indicating that it exists in soln. practically completely in the monomol. form, as is also indicated by mol. wt. detns. The majority of chemists probably feel that when 2 atoms, A and B, form a compd. A-B, both atoms bring into play amts. of energy which may differ according to the nature of the compd. formed but which are always equal to each other, while modern theoretical physics, in order to picture its conception of at. structure, has repeatedly compared the atom to a planetary system; thus, the "firmness of union," K , between 2 atoms may, for the sake of illustration, be represented by the equation $K = mm'/d^2$, where the product mm' is const. but m need not necessarily equal m' . Now, A may be considered as a triphenylmethyl, $\text{Ph}_3\text{C}'$, in which one of the Ph groups has been replaced by Ph_3C , i. e., A may be represented by the formula $\text{Ph}_3\text{C}'\text{C}'\text{Ph}_3 \dots$. The behavior of Ph_3C shows beyond doubt that the free 4th valence of the central C atom represents a materially smaller amt. of affinity than an ordinary C valence. Assuming that this relatively small amt. of affinity of the C' atom consumes an equally small amt. of affinity of the C' atom combined with it in A, it follows that after the satisfaction of this union the C' atom should have available a relatively larger amt. of affinity for its other 3 valences and that therefore its 4th valence (represented by the dotted line in the formula) should be stronger than the free valence of the central C atom of a Ph_3C radical. This is contrary to all the exptl. evidence. A is not only, unlike Ph_3C , practically monomol. in solns. but its residual valence is so small that the $\text{Ph}_2\text{CCPh}_2\text{Cl}$ obtained by satg. this valence with Cl, is unlike the stable Ph_3CCl , extremely labile and even at the temp. of boiling Et_2O already markedly decomp. into A. It is therefore concluded that in a C-C union the two atoms need not participate equally in the energy holding them together. S. and M. by no means imply, however, that chem. unions can be explained completely by old well known phys. laws; there are many other factors which cannot yet be formulated quant.

C. A. R.

Analogs of pentaphenylethyl. W. SCHLENK AND HERMANN MARK. *Ber.* 55B, 2299-302 (1922).—In attempts to prep. 'biphenylenetriphenylethyl, in order to det. what influence on the position of the equil. $2\text{R}_3\text{C} \rightleftharpoons \text{R}_3\text{CCR}_3$ would be exerted by the substitution of biphenylene for Ph groups in Ph_2CCPh_2 (preceding abstr.), only the

compound $\text{Ph}_3\text{CC} \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array}$ (A) could be obtained by the method used in making the

Ph_2CCPh_2 . Instead of the hoped-for products, $\text{Ph}(\text{C}_6\text{H}_4)_2\text{CNa}$ with Ph_2CCl_2 gave practically only $\text{Ph}_2\text{C}:\text{CPh}_2$ and $\text{Ph}(\text{C}_6\text{H}_4)_2\text{CC}(\text{C}_6\text{H}_4)_2\text{Ph}$ (B), and with $(\text{C}_6\text{H}_4)_2\text{CCl}_2$ yielded $(\text{C}_6\text{H}_4)_2\text{C}:\text{C}(\text{C}_6\text{H}_4)_2$ and B. The A, from Ph_3CNa and $(\text{C}_6\text{H}_4)_2\text{CCl}_2$, sep. in violet

prismatic crystals, mol. wt. in freezing C_6H_6 391–5 (i. e., like Ph_3CCPh , it is completely monomol. in soln. and, judging from the color of the crystals, also in the solid state), is immediately decolorized by Cl, the original color being restored by shaking with Cu bronze; the chloride is as easily hydrolyzed as $Ph_3CCPhCl$; it dissociates in sunlight at room temp. into Cl and the free A and is regenerated when the dissociated soln. is kept in the dark. C. A. R.

Free radicals and the changing value of the affinity of the carbon bond. W. SCHLENK. *Rec. trav. chim.* 41, 561–4(1922).—See preceding abstrs. E. J. W.

Condensation of α -halogen ketones with aldehydes. K. HUGO BAUER AND FRITZ WERNER. *Ber.* 55B, 2494–500(1922).—Widman found that $BrCH_2COPh$ and $ClCH_2COPh$ condense with aldehydes in the presence of $NaOEt$ with elimination of the halogen and formation of benzoyloxidoethanes, $BzCH_2CHRO$ (C. A. 10, 1526). If

the condensation is carried out in $AcOH$ with HCl or HBr as the condensing agent, it proceeds normally without elimination of the halogen, yielding α,β -unsatd. α -halogen ketones, which in some cases add the halogen acid and pass over into α,β -dihalogen ketones. Difficulty was experienced in finding a suitable solvent for recrystn. of the product obtained from BzH and ω -bromoacetoveratrone (A) in HCl - $AcOH$ and when C_6H_5N was used the cryst. product proved to be, not the expected $(MeO)_2C_6H_4COCHBr:CHPh$ (B) or $(MeO)_2C_6H_4COCHBr:CHCIPh$ (C) but $(MeO)_2C_6H_4COCH:CCIPh$ (D), whose formation can be explained only by elimination of HBr under the influence of the C_6H_5N from C. ω -Chloroacetoveratrone (E) and p - $Me_2NC_6H_4CHO$ yield $(MeO)_2C_6H_4COCCl:CHC_6H_4NMe_2$ (F), and as the product was recrystd. from alc. there presumably is no HCl addn. in this condensation. The same is true of $ClCH_2COMe$ and $Me_2NC_6H_4CHO$, except that in this case there is obtained a mixt. of the 2 condensation products $Me_2NC_6H_4CH:CClCOMe$ (G) and $Me_2NC_6H_4CH:CClCOCH:CHC_6H_4NMe_2$ (H), sepd. by means of their differing soly. in alc. In G the Cl is so firmly held that a further condensation to H can be effected in alk. as well as in acid soln. Chalcone dibromide, needles from alc., m. 158–9°, is obtained by allowing 10 g. $BrCH_2COPh$ in 30 cc. $AcOH$, 3 g. BzH and 30 cc. $AcOH$ - HBr , to stand 1–2 hrs. in a well closed flask with frequent shaking, 3',4'-Methylenedioxychalcone dibromide, from $BrCH_2COPh$ and piperonal with HBr - $AcOH$ or from $CH_3O_2C_6H_3CH:CHCOPh$ and Br in CCl_4 , leaflets from ligroin- C_6H_6 , m. 152°. 3,4-Dimethoxychalcone dichloride, scales from $MeOH$, m. 133–5°. 3,4-Dimethoxy-4'-dimethylamino- α -chlorochalcone (F), intensely yellow leaflets from dil. alc., m. 129–30°. 3,4-Dimethoxy- β -chlorochalcone (D), cubes from dil. C_6H_5N , m. 108–9° (in the exptl. part of the paper this is given the name and formula of the α -Cl compd., $(MeO)_2C_6H_4COCCl:CHPh$, but the discussion in the theoretical part seems to leave no doubt that the β -compd. is meant.—ABSTR.). α -4-Dimethylaminobenzal- α -chloroacetone (G), yellow leaflets from alc., m. 115°, sol. in dil. HCl or H_2SO_4 without color; semicarbazone, m. 202–3°; phenylhydrazone, fine faintly yellowish needles from C_6H_6 , m. 206–8°, decomp. easily. α,α' -Bis- p -dimethylaminobenzal- α -chloroacetone (H), m. 225°, almost insol. in alc., sol. in acids without color. p -Dimethylamino- α,α' -dibenzal- α -chloroacetone, from G, BzH and $NaOH$ in alc., dark brick-red leaflets from $EtOH$ - C_6H_6 , m. 150–1°, shows deep orange-red halochromism, dissolves in dil. mineral acids without color. α - p -Dimethylaminobenzal- α' -piperonal- α -chloroacetone, similarly obtained from piperonal, dark brick-red leaflets from $EtOH$ - C_6H_6 , m. 186.5°, shows a deep dark violet halochromism with concd. H_2SO_4 , dissolves in dil. acids without color. C. A. R.

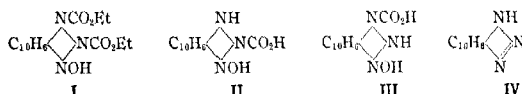
2,6-Dimethylnaphthalene. FRITZ MAYER AND ERIKA ALKEN. *Ber.* 55B, 2278–85 (1922).—2,6- $C_{10}H_8Me_2$ (A) in $AmOH$ slowly treated with 2 atoms Na, poured into H_2O , sepd. from the aq. layer, dried with KOH and again treated with 2 atoms Na gives $\Delta^{2,3}$ -dihydro-2,6-dimethylnaphthalene, b_{11} 125–6°. forms no picrate in alc. 1-Nitro-2,6-

dimethylnaphthalene (B) (11 g. from 10.4 g. A in 50-60 g. AcOH treated dropwise at 70° with 4.2 g. HNO₃ (d. 1.51) and stirred 2 hrs.), yellow leaflets from AcOH, m. 68°; 10 g. with SnCl₂ and HCl gives 3.4-4.0 g. of the *1-amino compound*, needles from alc., m. 91°, whose *acetyl derivative*, silky needles from AcOH, m. 211°, and *benzoyl derivative*, brown leaflets with silvery luster from xylene, m. 219-20°. Further nitration gives two different *dinitro derivatives* (1,4 and 1,5), according as it is carried out in H₂SO₄ or AcOH. Thus, 3 g. A in 80 cc. concd. H₂O₄ in ice treated with 1 g. HNO₃ (d. 1.51) in 30 g. H₂SO₄ and stirred 0.5 hr. gives 2 g. of a di-NO₂ compd., needles from AcOH, m. 186°, while in AcOH is obtained an isomer, fine yellow needles from AcOH, m. 179°, reduced in alc. by SnCl₂ and HCl to the *diamino compound*, dark red crystals from ligroin, m. 158-9°, whose *diacetyl derivative*, light yellow needles from AcOH, m. above 270°. The mother liquors from the di-NO₂ compd. prepd. in AcOH yield a *trinitro derivatives*, fine light yellow needles from AcOH, m. 243°. The entrance of a NO₂ group in the *o*-position to the Me in A renders this group mobile, so that 10 g. A added to 2.3 g. Na in 23 g. abs. alc. and 7.4 g. (CO₂Et)₂, refluxed 15 min., cautiously decompd. with H₂O and a little NaOH, filtered and pptd. ice-cold with dil. HCl yields 5-6 g. [*1-nitro-6-methylnaphthyl-2*]-pyruvic acid (C), light brown needles from AcOH, m. 195°; *methyl ester*, stout brown needles from ligroin, m. 119°; *oxime*, yellow needles from AcOH, m. 176°. The crude C (5 g.) in 20 parts of cold 2% NaOH treated with O₃ until the soln. no longer becomes lighter in color yields 2-3 g. [*1-nitro-6-methylnaphthyl-2*]-acetic acid (D), yellow crystals from AcOH, m. 201°; *methyl ester*, brownish crystals from xylene, m. 89°. With 4 g. KMnO₄, 5.5 g. C in 1.6 g. NaOH in 100 cc. cold H₂O gives 3 g. *1-nitro-6-methylnaphthalene-2-carboxylic acid*, needles from AcOH, m. 238-9°, reduced by FeSO₄ to the *1-amino acid*, light yellow needles from AcOH, m. 205-7°. From 1.4 g. NaNO₂ in a little H₂O added to a hot suspension of 5 g. C in 50 cc. H₂O and 15 g. of 10% HCl is obtained [*1-nitro-6-methylnaphthyl-2*]-acetonitrile, light yellow needles from MeOH, m. 162°, hydrolyzed by boiling Ba(OH)₂ to D; M. and A. believe that the HNO₂ is reduced to NH₂OH, which forms the oxime of C, and that this then decomp. into the above nitrile, CO₂ and H₂O. With FeSO₄ and NH₄OH, C gives *7-methyl- α -naphthindole-2-carboxylic acid*, needles from CHCl₃, m. 211°, which, heated 15 min. at 220°, yields *7-methyl- α -naphthindole*, brownish crystals from MeOH, m. 143°. When 5.3 g. C in 10 g. of 20% NaOH and 300 cc. H₂O is distd. with steam as long as any B passes over, then acidified, boiled with NaHSO₃ and decompd. in the cold with dil. H₂SO₄ there is obtained the yellow [*1-nitro-6-methylnaphthyl-2*]-acetaldehyde, m. about 212-3°, isolated as the *phenylhydrazone* (0.5-1.0 g.), light yellow leaflets from alc., m. 156°. If the decompn. of the NaHSO₃ soln. is effected at the boiling temp. or if the filtrate from the ppt. produced by decompn. in the cold is evapd. the product is *7-methyl- α -naphthi-satin*, fine red needles from AcOH, m. 265°; *phenylhydrazone*, red needles from alc., m. 275°. *7-Methyl- α -naphthoxindole*, from D with FeSO₄, dark brown crystals from AcOH, m. above 280°.

C. A. R.

Structure of the compounds formed in the oxidation of the β -naphthylamine-azo ester addition products. OTTO DIELS and HAROLD WACKERMANN. *Ber.* 55B, 2443-50 (1922).—The addn. product (A) of β -C₁₀H₇NH₂ to (NCO₂Et)₂, for which the structure 2,1-C₁₀H₆(NH₂)N(CO₂Et)NHCOC₂H₅ has been established with certainty (C. A. 15, 2086), gives on oxidation a bright yellow compd. (B) to which was assigned the constitution I. As this seems rather unusual, a no. of further expts. has been made to test its correctness. The Me analog of A, from (NCO₂Me)₂, likewise yields a yellow oxidation product (C); that this contains a mobile H atom is shown by the fact that it forms a well defined cryst. addn. product with EtO₂CNCO and yields a PhCH₂ deriv. On cautious treatment with dil. alkalis both B and C are hydrolyzed, lose 1 mol. CO₂ and yield the same monobasic acid (D). If I is the correct formula for B, D should have the

structure II or III. III is excluded, for such a compd. should at once lose H_2O and CO_2 to form the known 1,2-azimidonaphthalene (IV). The reason D, having the structure II, does not lose CO_2 and H_2O is probably that the OH and CO_2H groups on adjacent N atoms hold each other; the union is, moreover, a loose one, for treatment with concd. aq. NH_3Me results in the loss of CO_2 and H_2O and formation of IV. Likewise C is normally methylated by CH_3N_3 with evolution of N, but the Me ether which is undoubtedly first formed immediately loses CO_2 and, presumably, Me_2O and yields *N*-carboxymethyl-1,2-azimidonaphthalene (E), also obtained from IV and ClCO_2Me . All these facts are in harmony with the structure I for B and C and the oxidation of A may be conceived as consisting in a conversion of the two H atoms of the NH_2 group into HIO groups, followed by elimination of H_2O and ring formation. C, obtained in 6 g. yield



from five 2-g. portions of the $(\text{NCO}_2\text{Me})_2$ addn. product of $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$, each cautiously treated in 4 cc. gently boiling AcOH with H_2O_2 and allowed to cool after 2 min., brown-yellow prisms with bluish surface luster from MeOH , m. 117° (decomp.). *Carboxyethyl isocyanate addition product* (1 g. from 1 g. C and 0.8 g. EtO_2CNCO gently warmed together), m. 138° . *Benzyl ether* (0.9 g. from 1 g. C in Et_2O treated with 0.2 g. K in $\text{EtOH-Et}_2\text{O}$ and then refluxed 2-3 hrs. with 0.4 g. PhCH_2Cl), m. 187° . D (1.5 g. from 3 g. C in 15 cc. H_2O shaken a few min. with 3 cc. of 33% NaOH), pale yellow needles from $\text{C}_6\text{H}_5\text{-MeOH}$, m. 128° ; 1 g. slowly treated with about 1 cc. of 40% NH_2Me gives 0.3-0.4 g. IV, m. $178-9^\circ$. E (0.6 g. from 1 g. C in Et_2O with CH_3N_3), thick, faintly red-brown prisms from MeCN , m. $132-3^\circ$, also obtained in 0.3 g. yield from 0.5 g. IV boiled 5-10 min. in 5 cc. C_6H_6 and 0.3 g. $\text{C}_6\text{H}_5\text{N}$ with somewhat more than the calcd. amt. of ClCO_2Me . C. A. R.

ar-Aldehydes of tetrahydronaphthalene. KARL FLEISHER and GREGER FELDMEIER. *Ber.* 55B, 3290-3 (1922); cf. v. Braun, et al., *C. A.* 16, 4202.—5,6,7,8-Tetrahydro- α -naphthaldehyde (A), and the isomeric β -naphthaldehyde (B) were made from the resp. tetrahydromethylnaphthalenes by oxidation with CrO_3Cl_2 ; the yields were 10% and 4%, resp. A, b₁₄ $130-40^\circ$ (135°), gave a white cryst. bisulfite compound. B, b₁₄ $150-5^\circ$, formed a bisulfite compound, and a semicarbazone, white needles from alc., m. $221-3^\circ$, but gave no derivs. with $\text{NH}_2\text{NHCSNH}_2$, PhNH_2 , or PhCH_2CN .

BEN H. NICOLET

Pyroles. III. Ketones, ketonic acid esters and ketonic acid nitriles of substituted pyrroles. HANS FISCHER, KARL SCHNELLER and WERNER ZERWECK. *Ber.* 55B, 2390-403 (1922).—For further syntheses for the elucidation of the constitution of the cleavage products of pyrrole pigments and for degradation expts. the Hoesch ketone synthesis has been applied to substituted pyrroles along with the Gattermann HCN-aldehyde synthesis; these syntheses often proceed very smoothly. MeCN and PhCN have been combined with 2,4-dimethyl-3-carboxoxypyrrole (A), through the imide chlorides, to the corresponding ketones, which will next be reduced to the hydrois and then condensed with pyrroles to dipyrromethanes. With $(\text{CN})_2$ it had been hoped to obtain dipyrrol diketones, but in the only case in which the reaction has been carried out (with A), condensation took place with only one-half of the $(\text{CN})_2$ mol., giving 2,4-dimethyl-3-carboxoxypyrrol-5-glyoxylonitrile (B) in poor yield. $\text{CH}_3(\text{CN})_2$ likewise gave 2,4-dimethyl-3-carboxoxypyrrol-5-cyanoacetylpyrrole (C); the ester of the acid corresponding to this nitrile was obtained in good yield from A and $\text{NCCH}_2\text{CO}_2\text{Et}$. ClCH_2CN condenses in the same way with A and similar pyrroles; the Cl in the products is reactive

and can be replaced by NH_2 , Me_2N , MeNH and other groups; *2,4-dimethyl-3-carbethoxy-5-chloroacetylpyrrole* (D) with KCN gives C. ClCH_2CN yields with a hemopyrrole mixt. beautifully crystd. stable derivs., and it is hoped this will serve as a new method for sepg. such mixts. and especially for isolating β -methyl- β' -ethylpyrrole, of which no cryst. deriv. is yet known. Of special interest, naturally, are the pyrrolepropionic acids which are cleavage products of the blood and bile pigments and it had been hoped to obtain, through the Perkin or Erlenmeyer synthesis, phyllopyrrolecarboxylic acid from the trimethylpyrrolealdehyde, which, it seemed, should be easily obtainable by the Gattermann HCN synthesis. *2,4,5-Trimethylpyrrole* (E) does not condense well with HCN, $\text{NCCCH}_2\text{CO}_2\text{Et}$ and NCCO_2Et , however, but does with ClCH_2CN , and the Cl in the product can be replaced by CN, giving *2,4,5-trimethyl-3-cyanoacetylpyrrole* (F). *2,4-Dimethyl-3-carbethoxy-5-acetylpyrrole*, leaflets from alc., m. 142° , is obtained in good yield by treating 1 g. A and 0.5 g. MeCN in 5 cc. Et_2O for 4 hrs. with a slow current of HCl and heating the resulting imide-HCl (orange crystals from alc., m. 240°) 15 min. in H_2O on the H_2O bath. *5-Benzoyl analog*, needles from alc., m. 108° , forms faintly yellow solns., gives a negative reaction with Ehrlich's reagent (G) either hot or cold; the intermediate *imine hydrochloride*, obtained in 92% yield, lemon-yellow needles from alc., m. 228° , gives a faintly positive reaction with hot G. D, felted needles, m. 187° , gives a faint positive reaction with hot G (intermediate *imine hydrochloride*, obtained in 95% yield, m. 110°); *phenylhydrazone*, yellow needles from alc., m. 164° . *2,4-Dimethyl-3-carbethoxy-5-dimethylaminoacetylpyrrole*, from D and 33% alc. NHMe_2 heated 1 hr. in a sealed tube at 100° , m. 95° , gives a negative reaction with hot or cold G. *Ethyl 2,4-dimethyl-3-carbethoxypyrryl-5-acetate*, from A and $\text{NCCCH}_2\text{CO}_2\text{Et}$, felted needles from alc., m. 145° , gives a negative reaction with hot or cold G. B, leaflets with Ag luster from $\text{EtOH-H}_2\text{O}$, m. 165° , sol. in alc. with green-yellow, in Et_2O and CHCl_3 with pink, in Me_2CO , AcOH, $\text{C}_6\text{H}_5\text{N}$, C_6H_6 , dil. acids and alkalies on warming without color, gives a faint positive reaction with hot or cold G. C, faintly lemon-yellow needles from AcOH, m. 234° , generally forms faintly yellow solns., gives a positive reaction with cold G; yield, 70% from A and $\text{CH}_3(\text{CN})_2$ and almost quant. from D boiled 2 hrs. in alc. with 1 mol. KCN in a little H_2O . *2,5-Dimethyl-3-carbethoxy-4-chloroacetylpyrrole*, prepd. like D, m. 130° (yield, 75%); *intermediate imine hydrochloride*, stout yellowish needles. F, m. 178° . *Ethyl 2,4-dimethyl-3-carbethoxypyrrrole-5-glyoxylate*, obtained in 75% yield from A and NCCO_2Et , m. 82.5° , sol. in concd. HCl with dark red-violet color, hydrolyzed by cold 3.3% NaOH to the free acid, m. 192° (gas evolution). *Ethyl 2,5-dimethyl-3-carbethoxypyrrrole-4-glyoxylate* (yield, 97%), m. 102° . *Ethyl 2,4-dimethyl-3-acetylpyrrrole-5-glyoxylate* (yield, 84%), m. 120° ; free acid, m. 178° (gas evolution). From 2 g. crude hemopyrrole and 1.8 g. ClCH_2CN was isolated 1 g. of a *chloroacetyl derivative*, $\text{C}_{10}\text{H}_{11}\text{ONCl}$, faintly pink needles from dil. alc., m. 127° , 0.4 g. of which, heated 1.5 hrs. on the H_2O bath with 4 cc. HI (d. 1.96) and 8 cc. AcOH, yielded hemopyrrole, identified as the picrate, m. 121° . C. A. R.

Ketonanils. IV. The reduction products of ketonanils. E. KNÖVENAGEL (WITH J. MIL. KRAUCH). *Ber.* 55B, 2309-21 (1922); cf. C. A. 17, 92.—Reduction of $\text{Me}_2\text{C:NPh}$ with Na and alc. gives PhNH_2 and *2,2,3,3-tetramethylindoline* (A); that the product is not the isomeric *py-tetrahydro-2,2,4-* or *-2,4,4-trimethylquinoline* which might conceivably be formed is indicated by the following facts: It does not split off CH_4 with HCl (Bähr, C. A. 17, 92); the *N*-contg. nucleus is not dehydrogenated by $\text{Hg}(\text{OAc})_2$; A and its analogs described below show the strongly basic properties characteristic of the indolines, which are sol. in dil. AcOH; with HI and P the *N*-contg. nucleus of A can be ruptured with formation of a primary amine. The analogous reduction of *p*- $\text{MeC}_6\text{H}_4\text{N:CMe}_2$ with Na and alc., as also with Zn and HCl, yields *2,2,3,3,5-pentamethylindoline* (B). The reduction of α - $\text{C}_{10}\text{H}_7\text{N:CMe}_2$ (C) can be effected in stages; the first

product, obtained below 105° , is *acetone-ar-tetrahydro- α -naphthil* (D), while reduction with Na and AmOH under pressure gives *2,2,3,3-tetramethyltetrahydro- α -naphthindoline* (E), which is more strongly basic than the other indolines, its picrate not being hydrolyzed by hot H_2O . C, which is light yellow when pure, becomes deep dark brown after 24 hrs. in the light, while D becomes faintly brown only after 4 days and E shows traces of discoloration only after a long time. The odor of $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$ peculiar to C and, to some extent, to D disappears in E, which has a piperidine-like odor. A (13 g. from 20 g. $\text{Me}_2\text{C:NPh}$ in 250 g. alc. slowly treated with 20 g. Na), crystals from ligroin, m. 39.5° , mol. wt. in freezing C_6H_6 179–85, becomes faintly yellowish in the air, has a piperidine-like odor, gives no isonitrile reaction with CHCl_3 and K_2CO_3 , is insol. in NaOH, forms no carbonate, dissolves in cold 10% AcOH, the soln. becoming turbid on warming, is stable towards HCl gas even at high temps. ($240\text{--}80^{\circ}$); with III and P (Camozzi and Piccinini, *Gazz. chim. ital.* 28, II, 91(1898)) it gives, together with much of a strong base (presumably hydrogenated in the C_6H_5 nucleus) which forms a carbonate and gives no isonitrile reaction, a weaker base forming no carbonate, giving a distinct isonitrile reaction and yielding an Ac deriv. m. $146\text{--}7^{\circ}$. A reduces cold dil. alk. KMnO_4 ; its Et_2O and ligroin solns. have a faint bluish fluorescence; heated with $\text{CaH}_2(\text{CO})_2\text{O}$ and ZnCl_2 it gives a deep dark green color destroyed by NaOH and restored by HCl; with $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ it gives a red-brown, with $\text{FeCl}_3\text{-HCl}$ a green-blue, with excess of dil. HNO_3 a red color. *Hydrochloride*, m. $201\text{--}7^{\circ}$ (decompn.). *Picrate*, m. 74° , dissolves in about 160 parts cold H_2O . *Nitroso derivative*, from A in about 1 equiv. cold HCl with 1 mol. NaNO_2 , brown crystals from ligroin, dark green from alc., m. 44.5° , insol. in H_2O and NaOH, only slightly sol., but with deep dark brown color, in dil. HCl, soon blackens in the air; allowed to stand in Et_2O with HCl in abs. alc. it rearranges into *5-nitroso-2,2,3,3-tetramethylindoline hydrochloride*, voluminous green cryst. magma, sol. in H_2O with emerald-green color, begins to m. 170° (decompn.), can be nitrosated again to a brown flocculent mass giving the Liebermann reaction. *Acetyl derivative of A*, m. 83° . B (yield, about 95%), yellow oil stable to light, sol. in even warm dil. AcOH, dissolves in H_2SO_4 with a blue-green color becoming light brown on warming. *Hydrochloride*, m. $201\text{--}5^{\circ}$ (decompn.). *Acetyl derivative*, faintly yellow, m. 51° , b_{14-5} $165\text{--}7^{\circ}$, becomes more strongly yellow in the air, is sol. in hot dil. HCl and repptd. unchanged by NaOH. *Nitroso derivative*, light brown crystals from alc., m. 48.5° , dissolves in cold concd. HCl with gas evolution, without change in hot dil. HCl, being repptd. by NaOH. *Picrate*, red-brown substance from MeOH, m. 144° , hydrolyzed by hot H_2O . B gives no ppt. in alc. with $(\text{CO}_2\text{H})_2$ and can in this way be sepd. from *p-MeC}_6\text{H}_4\text{N:CMe}_2*. *Acetone- α -naphthil* (C), obtained in about 40% yield from $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$ and 0.5 mol. Me_2CO with a little I refluxed 6 hrs., viscous yellow oil, b_{12} $200\text{--}3^{\circ}$, gives a blue color in H_2O with oxidizing agents (FeCl_3 , AgNO_3), with EtNO_2 in alc. a red-yellow color changed to blue-violet by HCl, is sol. in dil. AcOH, forms no carbonate, is decompd. by refluxing 2 hrs. with 5 parts of 20% HCl into Me_2CO and $\text{C}_{10}\text{H}_7\text{NH}_2$. *Hydrochloride*, begins to decomp. 180° , m. 215° . *Acid oxalate*, almost pure white crystals from alc., m. 167.5° , assume a light blue coating in the air. *Picrate*, fine light yellow needles from H_2O , m. 210° (decompn.). D (21 g. from 30 g. C in 530 g. alc. slowly treated with 85 g. Na, the temp. being kept below 105°), b_{14-5} $193\text{--}6^{\circ}$, greenish yellow oil, gradually darkens in the air, forms no carbonate. *Hydrochloride*, m. 199° . *Acid oxalate*, needles from alc., m. $152\text{--}3^{\circ}$ (decompn.), becomes faintly yellowish in the air, is hydrolyzed by hot H_2O . *Picrate*, yellowish brown crystals from alc., m. $175\text{--}85^{\circ}$ (decompn.). Refluxed 1 hr. with 5 parts of 20% HCl, D gives Me_2CO and *ar-tetrahydro- α -naphthylamine*, identified as its di-oxalate, m. $159\text{--}60^{\circ}$. E (12 g. from 27 g. C in 60 g. AmOH treated with 30 g. Na without heating, then subjected to an extra pressure of 30 mm. Hg, treated with 70 g. more Na and heated vigorously 2.5 hrs.), light yellow oil slightly volatile with steam, insol.

in NaOH, reduces cold aq. alc. AgNO_3 but not Fehling soln., shows a faint bluish fluorescence, mol. wt. in freezing C_6H_6 227–34, b_{26} 200–5°. *Acid oxalate*, m. 183°. *Picrate*, brown, begins to darken 150°, m. 163°. C. A. R.

Arylated pyridines and their relations to the corresponding pyrylium compounds.

IV. W. DILTHER, J. NÜSSLEIN, HEINR. MEYER, AND H. KAFFER. *J. prakt. Chem.* **104**, 28–36(1922).—In continuation of earlier work (C. A. **15**, 3843; **16**, 2148) D. has shown weak basic properties in 2,4,5,6-tetraphenylpyridine (A) and even in pentaphenylpyridine (B). It was earlier thought that basicity disappeared in the triphenylpyridine (C) since its HCl salt could not be prepd. in H_2O . D. has prepd. both the HCl salt and picrate of C (from non-aq. solvents), the picrate of A (from Et_2O) m. 192°, and the perchlorate of B m. 299°. In contrast with the very weak basicity of B, pentaphenylpyrylium salts are all quite stable. In the course of this study D. has prepd. 2-p-bromophenyl-4,5,6-triphenylpyridine, m. 172°; picrate m. 226°; 2,6-bis-p-bromophenyl-4-phenyl pyridine, m. 196°; picrate, m. 212°; 2-[4-methoxy-3-methylphenyl]-4,6-diphenylpyridine, m. 112°; picrate, m. 223°; hydrochloride, m. 100–4°; 2-[4-hydroxy-3-methylphenyl]-4,6-diphenylpyridine, m. 151°; picrate, m. 232°; acetyl derivative, m. 101°.

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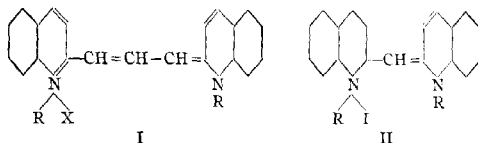
N,N'-Dialkyl[tetrahydro- γ,γ' -dipyridyls]. BRUNO EMMERT AND OTTO VARENKAMP. *Ber.* **55B**, 2322–6(1922).—Dimroth and Frster (C. A. **16**, 3661) have shown that *N,N'*-diacetyl[tetrahydro- γ,γ' -dipyridyl] (A), and γ,γ' -dipyridyl (B) in hot Ac_2O yield $\text{C}_8\text{H}_8\text{N}$ and diacetyl[dihydrodipyridyl]; they assume that the A is oxidized to $\text{C}_8\text{H}_8\text{N}$ and the B reduced to dihydrodipyridyl, which is simultaneously acetylated. If the *N,N'*-dialkyl[tetrahydro- γ,γ' -dipyridyls] (C) (C. A. **16**, 3901) also show a tendency to undergo this reaction, the following possibility must be reckoned with: the C can under certain conditions convert the dialkylidides of B, by removing the I atoms, into *N,N'*-dialkyl[dihydrodipyridyls] (D) while they themselves, by adding the two I atoms, are decompd. into 2 mols. alkylpyridinium iodides (E). As a matter of fact, a hot alc. soln. of *N,N'*-dibenzyl[tetrahydro- γ,γ' -dipyridyl] (F) treated with the equiv. amt. of B di[benzyl iodide] (G) assumes the deep blue color peculiar to D or a quinhydrone-like compd. of D; on shaking with air or addn. of I the color disappears without returning on standing. From the blue soln. could be isolated the expected E and a cryst. deep violet product (H) imparting to hot alc. and other solvents the characteristic blue color destroyed by air. The compn. of different samples varied but indicated a merquinoid substance $\text{C}_{18}\text{H}_{14}\text{N}_4\text{I}_2$, contg. to 1 mol. of a quinone-like D 1 mol. of G, i. e., only 0.5 of the added G had been converted into the D and the other 0.5 had added to this D, and unchanged F ought still to be present. Addn. of 2 mols. of G hardly increased the yield of H, however; there remained unchanged G. No explanation of this fact can be given. Weitz and Ludwig (C. A. **16**, 2516) found that their D takes up 2 atoms of I in hot Me_2CO or CHCl_3 , giving G in good yield. H in hot alc. absorbs 50–75% of the amt. of I calcd. for this component, and yields G, but as much amorphous material is formed at the same time, it is probably produced chiefly from the salt-like component. H can also be obtained simply, although not so pure, by shaking G with Na-Hg. The H often shows a well defined cryst. form (tablets) under the microscope and then has a strong dark bronze surface luster; when dry, it is quite stable in the air; it m. 180–5° on rapid heating; it dissolves in alc., PhNH_2 , $\text{C}_6\text{H}_5\text{N}$ and Ac_2O with deep blue color, changing to brown on shaking with air. C. A. R.

Di- and triquinolymethanes joined through the pyridine nucleus. III. Symmetrical di-2-quinolyl ketone. GÜNTHER SCHEIBE AND GUSTAV SCHMIDT. *Ber.* **55B**, 3157–60(1922); cf. C. A. **15**, 3110.—Di-2-quinolyl ketone (A) possesses a certain interest since Besthorn (*Ber.* **37**, 1237) prepd. a dye having the empirical compn. of such a compd. A is readily prepd. by allowing a soln. of $(\text{C}_6\text{H}_5\text{N})_2\text{CH}_2$ in 50% EtOH contg. a trace of

HCl to stand in the air for 2 weeks. It forms colorless prisms, m. 164°. It is obtained in a better yield by heating $(C_6H_7N)_2CH_2$ and $p\text{-ONC}_6H_4NMe_2$ in EtOH with a trace of alkali, forming a condensation product, $C_{22}H_{22}N_4$, yellow, m. 252°, and heating with AcOH or better with H_2SO_4 , giving A and $p\text{-H}_2NC_6H_4NMe_2$. A may also be prepd. by oxidizing the methane with dil. HNO_3 . Picrate, m. 179°. Phenylhydrazone, by heating in AcOH or EtOH with $PhNHNH_2$ or by coupling with PhN_2Cl , m. 190°. The oxime, prisms, m. 201°, was obtained by long heating in EtOH with $NH_2OH \cdot HCl$, or by the action of HNO_3 upon $(C_6H_7N)_2CH_2$. Anil, m. 161°. If A is heated with $PhNH_2$ at 120–30°, a compound contg. 2 mols. $PhNH_2$, m. 120°, is obtained.

C. J. WEST

Chemistry of the quinocyanines. Constitution of the pinacyanoles. W. KÖNIG. Ber. 55B, 3293–313 (1922).—K. favors the formula (I) of Mills and Hamer (C. A. 15, 829) for pinacyanoles, on both phys. and chem. evidence. The absorption spectra of



pseudoisocyanine salts (II) and I are extremely similar, showing all the same bands with only slight displacement; and I differs only by contg. a "streptostatic" (linearly disposed in the aliphatic chain) vinyl group. The synthesis of I (R = Me, or Et; X = I) confirms the structure given. The dicyanines are assumed to be α,γ -derivs. of similar type. The condensations involved are explained as due to a methylene tautomer of quinaldine. Some 30 structural formulas are given; also a new system of nomenclature for the cyanine dyes in general, which is of interest, but cannot well be abstracted. Pseudoisocyanine iodide (II; R = Me) was made by heating 2 g. α -chloroquinoline and 6 g. quinaldine-MeI 5 hrs. at 210° under pressure, treating with KOH in alc., distg. with steam, extg. the residue with Et_2O , drying, warming 2 hrs. with Me_2SO_4 , and later adding KI. The purification was complicated, but finally gave a 10% yield. Pinacyanole iodide (I, R = Et), also called 1,1'-diethyl-strepto-mono-vinylene-2,2'-quinocyanine iodide, formed when 6 g. quinaldine-EtI in 50 cc. hot Ac_2O was treated during 5 mins. with 2 g. $HC(OEt)_3$, and half the solvent then distd. off (yield 50%), m. 278° (decompu.). The corresponding N-Me₂ deriv. was prepd. similarly. The same products can be obtained by boiling the quinaldinium salt with $HC(OEt)_3$ in $PhNO_2$, or in C_6H_5N with $ZnCl_2$; $CHCl_3$, $CHBr_3$, or CHI_3 also may be used.

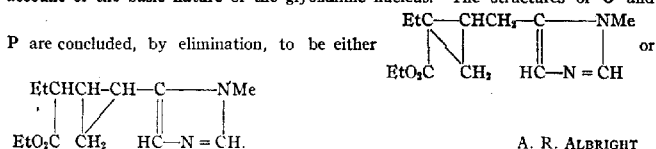
BEN H. NICOLET

Pilocarpine series. II. Pilocarpic esters and derivatives. MAX AND MICHEL POLONOVSKI. Bull. soc. chim. 31, 1185–1201 (1922); cf. C. A. 17, 395.—The lactonic nature of pilocarpine (A) and of isopilocarpine (B) has been established. In attempting to prep. esters of pilocarpic acid (C) from A with alc. and HCl gas, there were obtained instead the γ -Cl esters

$$\begin{array}{c} EtCHCH-CH_2C-NMe \\ | \quad | \quad || \\ RO_2C \quad CH_2Cl \quad HCN=CH \end{array}$$

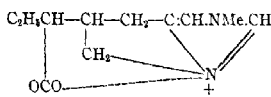
; this reaction is characteristic of γ -lactones. The chloro Me ester (D) is a thick oil which readily solidifies; after gentle trituration with EtOH it is obtained as small transparent prisms m. 42–4°, insol. in H_2O , or dil. alkalies, very sol. in EtOH, Et_2O , $CHCl_3$, and acids, α_D 32.6°, strongly basic, giving with acids well crystd. salts neutral to litmus. The nitrate (E) is slightly sol. in cold EtOH, crystg. in brilliant leaflets m. 175°, and having α_D 20° in H_2O . The Cl atom is removed by boiling with HNO_3 and $AgNO_3$; it is detd. by boiling with $EtONa$, evapg., heating with Na_2CO_3 , and weighing as $AgCl$. The Et chloro ester (F), prepd. in an analogous manner, is an oil having α_D 29.2° in EtOH. F nitrate (G) crysts. in

brilliant plates from abs. EtOH, m. 136°, α_D 23.4°, sol. in H₂O, slightly sol. in cold EtOH. Treatment of G with concd. H₂SO₄ yields *Et* γ -chloronitropilocarpate (H), a neutral oil sol. in Et₂O, and identical with the esterification product of nitropilocarpine. The dil. HNO₃ used in prepg. G effects a partial sapon., affecting both alkyl and halogen; some relactonization takes place, forming A, and, to a certain extent, isomerization to B also occurs; these products are found in the mother liquors from G; the latter phenomenon is quant., if alc. KOH be used as the hydrolyzing agent. *Methyl* γ -chloronitropilocarpate (I), made from B by a method similar to that used with A, is a thick oil of very alk. reaction, insol. in H₂O, sol. in all ordinary org. solvents, α_D -7.5° in EtOH; its *nitrate* (J) is very hygroscopic, crysts. badly from EtOH, m. approx. 100°, α_D -5.6° (0.694 g. in 20 cc. MeOH). The *Et* ester (K) is an oil having α_D -5°; its *nitrate* (L), very sol. in EtOH, Me₂CO, and H₂O, forms needle agglomerates, m. 95°, optically inactive. K is more readily sapond., even by dil. HNO₃, than the corresponding deriv. of A. The tendency to ready relactonization is characteristic of γ -halogenated aliphatic acids, a furan ring being formed; the mechanism involves first sapon., then loss of HCl, the lactone resulting. This decompn. takes place even in the cold, and without a solvent, the products including a small amt. of A, unchanged K, and the HCl salt of a quaternary base which liberates NH₃ and A on treatment with alkali; the mechanism of the formation of the quaternary base is uncertain. Cryst. salts of the Cl esters are stable. 2.72 g. F in 20 cc. abs. EtOH gave, on heating 4 hrs. with 10 cc. N EtONa and freeing from NaCl, small proportions of B, its Na salt, the Na salt of a new acid resulting from the sapon. of the dechlorinated ester, and 2 basic esters which were sepd. by means of unequal solys. of their nitrates in EtOH; the less sol. is *Et* α -anhydripilocarpate *nitrate* (M), m. 165°, α_D -9° in EtOH and 3.4° in H₂O; the more sol. is the *nitrate* of *Et* β -anhydripilocarpate (N), m. 95°, α_D -28° in H₂O. The corresponding bases are, resp., *Et* α -anhydripilocarpate (O), an oil, and *Et* β -anhydripilocarpate (P), large transparent tables, m. 48°; the hydrochloride of O crysts. well and m. 122-5°. K under the same conditions gave the same 2 nitrates as the derivs. of A; F is probably at least partially isomerized simultaneously with loss of Cl. The mixt. of O and P was sapond. with Ba(OH)₂; removal of Ba and liberation of the acids yielded α -anhydripilocarpic acid (Q), less sol. in H₂O, white leaflets m. 243°, and β -anhydripilocarpic acid (R), more sol. in H₂O, brilliant prisms, m. 184°. Q is slightly sol. in Et₂O, somewhat sol. in EtOH, sol. in both acids and alkalies, although neutral to litmus; the acid salts are more stable than the basic; it gives a well crystd. hydrochloride, m. 187°, from abs. EtOH. Q has α_D -19° in H₂O; it is stable on heating above its m. p., or on heating with EtONa, Ba(OH)₂, or HCl, reduces KMnO₄ in the cold, because of the imidazole group, is very stable toward reducing agents. 0.24 g. O was brominated by slow addn. of 20 cc. 0.1 N Br in CHCl₃; the solvent was distd. after 12 hrs. and the pasty residue treated with a little H₂O, from which Et₂O removed a neutral oil which after sapon. with Ba(OH)₂ and acidification yielded a *brominated* α -anhydripilocarpic acid (S), m. 138-9° from EtOH. In the H₂O was found *Et* α -anhydripilocarpate *hydrobromide* (T), identified by conversion to M (m. 165°). The simultaneous formation of S and T proves that the bromination is a substitution, not an addn., reaction. R is very sol. in H₂O and EtOH; in H₂O it has α_D 42°; its hydrochloride m. 142°; its other properties are like those of Q. Q and R, C₁₁H₁₂N₂O₃, are true acids but have rather the character of NH₂ acids on account of the basic nature of the glyoxalinc nucleus. The structures of O and



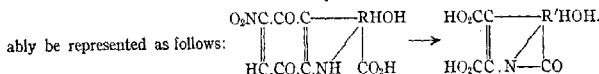
A. R. ALBRIGHT

Pilocarpine series. III. Isopilocarpine anil, or phenylisopilocarpyrrolidone. MAX POLONOVSKI AND MICHEL POLONOVSKI. *Bull. soc. chim.* 31, 1201-4(1922).—Pilocarpine-HCl, heated 40 mins. at 205-10° with a slight excess of PhNH₂, made alk. and steam-distd. to remove PhNH₂, treated with K₂CO₃ and extd. with CHCl₃, and this soln. then extd. with dil. NaOH to remove isopilocarpine, gave *isopilocarpine anil* (A), sol. in alc. or AcMe, insol. in H₂O or in hot Na₂CO₃. With dil. HNO₃, A gave the *nitrate*, leaflets from alc. or AcMe, m. 162°, sol. in H₂O, alc., or AcMe, [α]_D 21.2°. *Itydrochloride* (H₂O) forms white hygroscopic prisms from AcMe, m. 135°. Nitration of A seems to affect the Ph nucleus. **IV. Metapilocarpine.** *Ibid* 1204-8.—Pinner (*Ber.* 38, 2051(1905)) described metapilocarpine (B) as a new isomer. B is insol. in CHCl₃, and gives only MeNH₂ with concd. alkali. Pinner's data are confirmed, and the following properties added: B is insol. in Et₂O, ligroin, CHCl₃, very sol. in EtOH, AcMe, miscible with H₂O, but salted out by much K₂CO₃. It is optically inactive, neutral to litmus, and forms salts with acid reaction, none of which was obtained cryst. It is concluded that B is not a lactone, but probably a betaine:



BEN H. NICOLET

Strychnos alkaloids. XXXIII. Degradation of cacotheline by bromine. HERMANN LEUCHS, HANS MILDBRAND AND W. ROBERT LEUCHS. *Ber.* 55B, 2408-15(1922); cf. *C. A.* 16, 3664.—The yield of the acid (A) obtained by oxidation of cacotheline (B) with Br (Hanssen, *Ber.* 20, 452(1897)) has been increased from 15-20% to 35-8%. Dried at 100-30° under 15 mm. it loses 2, not 1, mol. H₂O and therefore has the compn. C₁₉H₂₉O₄N₂ (cf. Ciusa and Scagliarini, *C. A.* 5, 1279). Treatment of the filtrate with SO₂ gave 3% of a 2nd degradation product as a loose SO₂ compd., which on recrystn. yielded a S-free *hydrobromide* C₁₇H₂₉O₄N₂Br₂·HBr (C); the free base on boiling with H₂O changes into another form with ionized Br but with boiling HBr regenerates the original HBr salt. A behaves towards alkalis as a monobasic acid, yet in the HBr salt holds the HBr so firmly with its basic N that it is hardly pptd. by cold AgNO₃ and the salt can for the most part be recrystd. unchanged after addn. of 1 mol. alkali; only from hot soln. was it possible to ppt. a part of the Br-free base with alkali. The CO₂H group which can be detected by titration and by means of the mono-Ag salt can also be esterified; more vigorous treatment with MeOH and HCl gives a di-Me ester. As found by H., an ester of A cannot be obtained from the Ag salt with MeI; A, however, is not regenerated, but there is formed, in good yield, a *methylbetaine* (D), the MeI adding on the basic N atom and the I being split off as AgI: ≡NMeI + AgO₂C— = ≡NMeOCO— + AgI. In A, therefore, 4 of the O atoms are present in CO₂H groups, and the 2 others and one of the N atoms are probably present in the amide and sec. alc. groups of the brucine, as A does not react with aldehyde and ketone reagents. The oxidation may probably be represented as follows:



A would then be a kind of maleic acid. It has thus far not been possible to obtain an anhydride from it, but the presence of a reactive C:C bond is shown by the fact that with Na-Hg it smoothly adds 2, and only 2, atoms of H, yielding a *product* (E) isolated as the *dimethyl ester* (E). A striking point in the above scheme is that R' (= C₁₄H₂₅N) must contain 2 more H atoms than R; these 2 atoms can have been added only by an

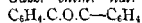
unusual reaction. **B** itself on boiling in H_2O is autoreduced to the dihydro compd. but the position which takes up the H is no longer present in **A**. From 10.16 g. **B** in 200 cc. H_2O and 3 cc. Br in 20 cc. HBr (d. 1.46), gently heated 15–30 min. on the H_2O bath, then boiled 15 min. (adding 0.4–0.8 g. more of Br if necessary) and allowed to stand several hrs. in ice is obtained 3.5–3.8 g. **A**. HBr, slender prisms and rectangular, striated leaflets with $2\text{H}_2\text{O}$ from H_2O -HBr, sol. in 13 parts boiling H_2O , in 52–3 parts of *N* HBr; the filtrate from the crude salt, satd. in ice with SO_2 and allowed to stand 1–3 days in the ice box gives 0.65 g. of the SO_2 compd. of **C** as 6-sided leaflets. Free **A**, obtained in about 50% yield by evapp. the soln. of the HBr salt in 1 mol. NaOH, seps. from hot soln. with $2\text{H}_2\text{O}$, at 0° in fine needles with $6\text{H}_2\text{O}$, easily sol. in warm H_2O until the prisms or 4–6 sided tables of the dihydrate, which require 26–7 parts of H_2O at 100° for soln., sep. **A** reduces neither $\text{NH}_3\text{-AgNO}_3$ nor Fehling soln.; it reacts and tastes acid, dissolves easily in NaHCO_3 and alkalis, $[\alpha]_D^{14} -37.0^\circ$ (in 1 mol. of 0.1 *N* NaOH); Ag salt (2.5 g. from 3 g. of the HBr salt in hot H_2O with Ag_2CO_3), silky needles sol. in about 15 parts cold H_2O and sepp. from less than 3 parts hot H_2O as a gel which later crystals, sensitive to light when moist or in soln., especially on heating; *hydrochloride*, needles or prisms with about $3\text{H}_2\text{O}$ from 5 *N* HCl, sol. in less than 10 parts *N* HCl, seps. from hot H_2O in tables, later in needles; 1 g. dissolves in 15 cc. hot MeOH, at first easily until there sep. prisms which lose 9.64% in wt. at 100° , dissolve only in 60 parts boiling MeOH and then at 0° sep. in fine needles losing 8.9% in wt. at 95° , which dissolve easily in warm MeOH but soon sep. again in prisms. *Acid sulfate*, long slender prisms or needles with $3\text{H}_2\text{O}$ from 2.5 *N* H_2SO_4 sol. in less than 4 parts H_2O at 100° , at once gives a ppt. with cold BaCl_2 . *Nitrate*, 4-sided tables and rhombohedrons or rectangular prisms with $1\text{H}_2\text{O}$, sol. in 10 parts boiling H_2O , $[\alpha]_D^{20} -30.0^\circ$ (H_2O). **D**, $\text{C}_{20}\text{H}_{24}\text{O}_8\text{N}_2$ (1.4 g. from 2.4 g. of the Ag salt in 240 cc. MeOH and 2.4 cc. MeI allowed to stand 10–5 min. with frequent shaking), prisms losing 15.8–16.6% in wt. at 100° under 15 mm., easily sol. in cold H_2O with acid reaction, $[\alpha]_D^{18} -5.6^\circ$ (H_2O); there is also obtained 0.2–0.3 g. of difficultly sol. prisms losing 6.4–16.7% in wt. at 100° which seem to consist either of an isomeric betaine or of **A**; they yield with HNO_3 prisms of a difficultly sol. nitrate with 7.75% H_2O , $[\alpha]_D^{19} -30.8^\circ$ (H_2O). From 0.15 g. **D** with 2 cc. H_2O and 1 cc. HI (d. 1.6) dissolved in 20 cc. boiling H_2O , decolorized with 1 drop H_2SO_3 and cooled to 0° is obtained 0.15 g. of the *methiodide* of **A**, faintly yellowish needles and prisms with $2\text{H}_2\text{O}$, very difficultly sol. in cold H_2O with acid reaction. *Monomethyl ester hydrochloride* of **A** (0.4 g. from 0.5 g. **A** dissolved at 20° in 12.5 g. MeOH with 20% HCl and at once evapd. over KOH and H_2SO_4), needles from MeOH; free *ester*, amorphous, easily sol. in H_2O with neutral reaction; *methiodide*, from the ester and MeI in MeOH (yield, 40%), broad yellowish prisms from 75% MeOH, loses 0.95–3.4% in wt. at 100° under 15 mm., has an acid reaction in H_2O . *Dimethyl ester hydrochloride* (1.4 g. from 2 g. **A** allowed to stand 1–2 days in 60 cc. MeOH half-satd. with HCl), stout rectangular prisms losing 12.2–13% in wt. over P_2O_5 at 65° ; free *ester*, prisms with strong alk. reaction from H_2O , m. $153\text{--}5^\circ$ (foaming); *methiodide*, thick 6-sided tables from H_2O , small 5-sided leaflets from MeOH, reacts neutral in H_2O . **E**, $\text{C}_{19}\text{H}_{23}\text{O}_8\text{N}_2$ (4.5–5.0 g. from 6 g. **A**-HBr in 120 g. H_2O at 0° treated with two 24-g. portions of 2.3% Na-Hg* then with 10 cc. of 5 *N* HCl, evapd. *in vacuo* and satd. in 100 cc. MeOH at 0° with HCl), prisms from Me_2CO or AcOEt, loses 3.2% in wt. at 65° under 15 mm. (at 100° *in vacuo* it undergoes chem. change), sinters 138° , m. $143\text{--}7^\circ$ (foaming), *in vacuo* at about $132\text{--}5^\circ$, moderately sol. in cold H_2O with alk. reaction, forms easily sol. salts with H_2SO_4 and HCl; *hydrobromide*, prisms; *nitrate*, stout prisms from dil. HNO_3 , stout prismatic columns from H_2O ; *hydrochloride*, rectangular prisms or leaflets from MeOH, loses 3.85–4.0% in wt. at 65° under 15 mm., sol. in about 10 parts hot MeOH; *methiodide* (0.6 g. from 0.7 g. **E**), small prisms or stout, elongated rectangular tables, loses 2.04–2.66% in wt. at 65° under 15 mm., very easily

sol. in H_2O with neutral reaction. Free acid hydrochloride, from $E \cdot HCl$ allowed to stand overnight in 10 parts of 12 $N HCl$ and evapd. *in vacuo* at $50-60^\circ$, quadrate leaflets with 3 H_2O . **C** (0.3 g. from 0.6 g. of the SO_2 compd. heated 0.5 hr. at 100° with 10 parts of 2 $N HBr$), loses 2.7–2.9% in wt. at 100° under 15 mm., dissolves in 8 parts boiling H_2O , in 22 parts boiling N acid, from which it seps. in 6-sided tables or prismatic needles, gives a ppt. with cold $AgNO_3$; nitrate (0.3 g. from 0.54 g. **C** in 5 cc. of 0.1 $N HBr$ with 0.25 g. $AgNO_3$ in 1 cc. of 5 $N HNO_3$), rectangular elongated leaflets and prisms, loses 3.2–3.3% in wt. at 100° under 15 mm., gives no ppt. with $AgNO_3$; free base, from **C** and $NaOH$ at 0° , amorphous powder changing to granular crystals, loses 2.2% in wt. at 65° *in vacuo*, gives no ppt. in HNO_3 with $AgNO_3$, dissolves in about 100 parts hot H_2O .

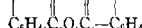
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Preparation and mechanism of formation of phenanthroxazine. B. FORESTI.

Gazz. chim. ital. **52**, II, 90–6(1922).—In the formation of phenanthroxazine



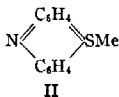
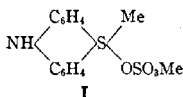
A from phenanthrenequinone with $PhNHNH_2$; Bamberger and



Grob (*Ber.* **34**, 533(1901)) considered that the phenanthrenehydroquinol (**A'**) and 9-amino-10-hydroxyphenanthrene (**B**) condense to give **A**. They also obtained **A** by treating **A'** in cumene with NH_3 gas and heating at $120-30^\circ$. F. found that when reducing phenanthrenequinone monoxime in boiling $EtOH$ with H_2S (Schmidt, *Ber.* **35**, 3130(1902)) **B** is easily obtained but the ppt. when freed from S with CS_2 gives a residue of **A** owing to condensation of **B**. 1 g. of the hydrochloride (**C**) of **B** boiled in 25 cc. $EtOH$ with a little excess fused $NaOAc$ in CO_2 12 hrs. gave a ppt. which was washed with H_2O to remove salts. The 0.65 g. residue was **A**, m. 422° . If the $EtOH$ is replaced with H_2O the formation of **A** is complete in 1 hr. When 2 g. **C** suspended in 70 cc. $PhNO_2$ is heated the soln. becomes clear in a few min. and when cooled after filtering hot seps. 0.5 g. **A**. Similar results are obtained with $C_6H_5I_3$ as solvent but if boiling is prolonged to 1–2 hrs. **A** is transformed completely into phenanthrazine (**D**), m. 440° . **D** is also obtained from **A** in $PhNO_2$ on boiling 1 hr. in the presence of NH_4Cl . Test expts. on the basis of the phenanthraquinone used show that the yield of **A** by this method is about the same as that obtained by **B** and **G**. **A** boiled 12 hrs. with aq. NH_4OH was recovered unchanged, which indicates that the action of NH_4OH on dihydroxyphenanthrene (**E**) (F., *C. A.* **16**, 2684) does not involve the primary formation of **B**, which in turn gives **A** and then **D** (the product obtained from **E**). **C** boiled for a long time with aq. NH_4OH does give a mixt. of **A** and **D**. E. J. WITZEMANN

Sulfonium bases which are derived from thiodiphenylamine and analogous compounds. F. KEHRMANN AND HENRI DARDEL. *Ber.* **55B**, 2346–56(1922).—The method of prep. salts of aromatic sulfonium bases by the action of Me_2SO_4 on aromatic sulfides with open chains has been extended to aromatic sulfides with S in a ring. Thus thiodiphenylamine (**A**) adds Me_2SO_4 at room temp., forming the salt **I**, which is converted by caustic alkalis into the corresponding colorless H_2O -sol. hydroxide; this easily loses H_2O with formation of the yellow unstable anhydride **II**, which is converted by CO_2 into the carbonate corresponding to **I**. Thiophenyl- α - (**B**) and - β -naphthylamines (**C**) and thioldi- α - (**D**) and - β -naphthylamines (**E**) behave in the same way towards Me_2SO_4 , but the anhydrides obtained from **D** and **E** are quite stable and can be isolated and analyzed. All these sulfonium bases, in the form of their hydrates, split off $MeOH$ on heating with H_2O , regenerating the original thioamine, and the halide salts likewise slowly lose alkyl halide at room temp. The anhydrides of type **II**, which are probably *o*-quinoidal, are peculiar in that they contain 4-valent S , all of whose available affinity is used to combine with C only. Their unsatd. nature is shown by their intense colors and by the ease with which they add H_2O or acids to regenerate the colorless satd. sul-

fonium compds. The long known *N*-Me derivs. of A and its analogs (Bernthsen, *Ann.* 230, 78(1885)), which are isomeric with the above yellow anhydrides, also easily add Me_2SO_4 on the S, yielding salts of the type I; the corresponding bases are likewise colorless and H_2O -sol. but do not form anhydrides; on heating in soln. they lose MeOH and regenerate the original *N*-Me compd. All the salts of type I thus far studied are extraordinarily sensitive to light, both in the solid state and in soln. Their solns. are intensely bitter, almost like those of quinine salts, and they are strong poisons. If, in the prepn. of A by Bernthsen's method, 0.1 g. I is added to a charge of 50 g. Ph_2NH and 20 g. S, the evolution of H_2S begins at 170° instead of 225° , and is complete in 0.5 hr. instead of 5-6 hrs., and the yield of recrystd. product is 82%. *S*-Methylthiodiphenylaminesulfonium perchlorate, obtained in 70% yield from 9.5 g. A and 7 g. Me_2SO_4 heated



1 hr. at 80° in a stoppered flask, poured into 0.5 l. H_2O , shaken with charcoal and treated with a few cc. of 25% HClO_4 , heavy cryst. powder, can be rapidly crystd. in small amts. without much decompn. from H_2O , forms a soln. neutral to litmus, is unchanged by Na_2CO_3 or NaHCO_3 but is turned yellow by NaOH , Et_2O extg. the yellow substance and being in turn decolorized by shaking with distd. H_2O , which regenerates the colorless base, although a part of the compd. is decompd. into A, which remains in the Et_2O . The yellow alk. soln. on short boiling soon deposits A. Cold concd. H_2SO_4 dissolves the salts of type I without color. *N,S*-Dimethylthiodiphenylaminesulfonium perchlorate, obtained in 65% yield from the *N*-Me deriv. of A heated 1 hr. at 90° with Me_2SO_4 , slender prisms slowly darkening in the light, is not colored by concd. alkalis and seps. unchanged if the soln. is sufficiently concd. but on boiling the original thioamine quickly seps.; the salt dissolves in cold concd. H_2SO_4 without color. C, flat S-yellow needles from ligroin, m. 178° , shows strong green fluorescence in soln., is obtained in 80% yield from $\beta\text{-C}_{10}\text{H}_7\text{NHPh}$, S and I heated 2 hrs. at 200° under 12-5 mm. *S*-Phenylthiophenyl- β -naphthylaminesulfonium perchlorate, obtained in 75% yield from C and Me_2SO_4 heated 1.5 hrs. at 70° , needles from H_2O , forms a colorless aq. soln. unchanged by Na_2CO_3 but at once turned lemon-yellow by NaOH , with formation of a yellow ppt. sol. in Et_2O ; the Et_2O soln. is almost entirely decolorized by aq. CO_2 with formation of a H_2O -sol. carbonate. *N,S*-Dimethyl homolog, obtained in 84% yield from the *N*-Me deriv. of C and Me_2SO_4 after 1 hr. at 110° , unchanged in H_2O by NaHCO_3 and by cold NaOH , but boiled 1-2 hrs. in the latter soln. it decomp. into the original thioamine; the salt dissolves without color in H_2SO_4 but quickly becomes superficially dark brown in the light. B, golden yellow leaves from ligroin, m. 130.5° , shows green fluorescence in soln., is obtained in 78% yield from $\alpha\text{-C}_{10}\text{H}_7\text{NHPh}$, S and I heated 1 hr. at 200° in *vacuo*; with Me_2SO_4 after 45 min. at 50° it yields 40% of *S*-methylthiophenyl- α -naphthylaminesulfonium perchlorate, partly decompd. by boiling with pure H_2O , pptd. by Na_2CO_3 to some extent, by NaOH completely, as the yellow anhydride, whose lemon-yellow Et_2O soln. is not decolorized by distd. H_2O until a drop of AcOH is added. E (85% from $(\beta\text{-C}_{10}\text{H}_7)_2\text{NH}$, S and I heated 0.5 hr. at 180°), light yellow needles from PhMe , m. 233° , shows green fluorescence in soln., gives with Me_2SO_4 after 5-6 hrs. at 85° 55% of *S*-methylthiodi- β -naphthylaminesulfonium perchlorate, cryst. powder; chloride, leaflets. Anhydride, from the methosulfate with NaOH - NaCl , light orange needles from CHCl_3 -ligroin, m. $160-5^\circ$ (partial decompn.). *N,S*-Dimethylthiodi- β -naphthylaminesulfonium perchlorate (30% from the *N*-Me deriv. of E and Me_2SO_4 after 2 hrs. at 120°). D, orange-yellow powder quickly turning superficially brown in the light, is

obtained in 60–70% yield from $(\alpha\text{-C}_{10}\text{H}_7)_2\text{NH}$, S and I heated 2 hrs., first at 150° , then at $170\text{--}80^\circ$, pptd. from CHCl_3 as the picrate and decompd. with excess of cold dil. aq. NH_4OH ; with Me_2SO_4 after 1 hr. at 80° it gives 50% *S*-methylthiodinaphthylamine-sulfonium perchlorate; anhydride, golden yellow needles from CHCl_3 -petr. ether, m. 141° .

C. A. R.

Trifluoroacetic acid. FRÉD. SWARTS. *Bull. sci. acad. roy. Belg.* 8, 343–70 (1922).—S. attempted to prep. $\text{CF}_3\text{CO}_2\text{H}$ (A) by fluorinating $\text{F}_3\text{CICCO}_2\text{H}$ and its ester (B), by replacing in B the Cl with I in the hope that I might be replaced by F more readily than would the Cl but B was stable toward KI in contact during 2 years. Oxidation of C_6BrF_3 (*Bull. sci. acad. roy. Belgique* 1899, 357) in an attempt to obtain $\text{F}_3\text{BrCCO}_2\text{H}$ gave very low yields. It has been found (C. A. 5, 3684) that a halogen atom adjacent to 2 F atoms cannot be replaced by F. The oxidation of trifluoromethylcyclohexane by HNO_3 can be effected on only a very small scale because of the pressures involved, but this idea suggested the possibility of obtaining A by the oxidation of cyclic compds. bearing the CF_3 group. Trifluorotoluidine (C) (*Bull. sci. acad. roy. Belgique* 1898) was oxidized with 8 mols. $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 . The mixt. was boiled for a week, then distd. and the distillate was neutralized with $\text{Ba}(\text{OH})_2$. BaSiF_6 and BaCO_3 were filtered out, the filtrate was evapd. to dryness, and taken up in boiling alc. 63 g. of the Ba salt of A were obtained; the orange-red crystals which sepd. in the condenser were trifluoroacetaldehyde (D), m. 82.3° , b. 283° , easily volatile in steam, very sol. in alc. and Et_2O , less sol. in petr. ether. The yield of A was about 6%. The best conditions for prep. A are given. KMnO_4 in an acid medium could not be substituted for CrO_3 . A was obtained by distg. the Na salt with H_2SO_4 in an app. from which H_2O was excluded, b. $72.4\text{--}2.5^\circ$. A was purified by crystn. in a closed vessel. The mother liquors were decanted through diverse side tubes; the product first obtained crystd. at -15.55° , rhombic plates, fuming strongly in the air and having an irritating odor; when applied to the skin caused burns. At 105.46° a mixt. contg. 79.4% of A distd. A table showing the acid content of the distillate resulting at various temps. is given, also a table showing the mol. cond.; $\mu_\infty = 382$ (from the cond. of the Na salt). A is a strong acid resembling $\text{ClFCHCO}_2\text{H}$, $\text{Cl}_3\text{CHCO}_2\text{H}$, and $\text{FBr}_2\text{CCO}_2\text{H}$. The salts of A are sol. and deliquescent. The Ag salt is sol. in C_6H_6 , being associated in this solvent. The salts resist the action of bases. HCF_3 was not formed, and only a small amt. of oxalate. The Ba salt and NaOH soln. were heated in an app. permitting the collection of evolved gas and during 2 hrs. heating the vol. of gas in the app. did not increase. Ethyl trifluoroacetate (E), obtained by distg. at $60\text{--}4^\circ$ the Na salt and alc. with H_2SO_4 , b. 61.7° , $d_{16.7} 1.1952$, $n_D 1.30783$, $n_D 1.31237$, $n_D 1.31527$. The refractive power is very low. Trifluoroacetic anhydride (J), prepd. by treating A with P_2O_5 at 100° , b. $39.5\text{--}40.5^\circ$. It solidifies in $\text{Et}_2\text{O}\text{--}\text{CO}_2$ mixt., m. -65° . The vapor d. detn. lead to the fact that it is non-associated. Trifluoroacetamide (F) was obtained by the action on E of NH_4OH soln. satd. at 0° . The mixt. was shaken with Et_2O , and F and the NH_4 salt of A were dissolved and this mixt. on distn. gave a residue from which F was sepd. by dry Et_2O . F was purified by soln. in CHCl_3 ; a 48% yield only could be obtained, pearly spangles, very sol. in alc. and Et_2O , slightly sol. in CHCl_3 , almost insol. in petr. ether, m. 74.8° , b. 162.5° , very sol. at ordinary temp. F could not be obtained by distg. the NH_4 salt of A. 1.7 g. trifluoroacetonitrile (G) results when 4.8 g. F are heated with 11 g. P_2O_5 . The condenser was held at -80° , G b. -61° (140° below MeCN), a gas, H_2O taking up 0.5 vol. and alc. 2 vols. KOH soln. when satd. with G and evapd. *in vacuo* gave the K salt of A. The NH_4 salt of A gave G on treatment with P_2O_5 . Trifluoroacetanilide (H) resulted when A was heated at 120° for 8 hrs. in tubes with PhNH_2 . The product distd. under atm. pressure gave after elimination of H_2O , H, b. $220\text{--}25^\circ$. It had the odor of carbylamine. CHF_3 was formed simultaneously with H according to the equation $\text{CF}_3\text{CO}_2\text{H} \longrightarrow$

$\text{CHF}_3 + \text{CO}_2$; Goldschmidt and Brauer observed an analogy in the case of $\text{CCl}_3\text{CO}_2\text{H}$ (*Ber.* **38**, 109 (1905)). H crystd. from warm aq. 60% alc. m. 87.64° (sublimes), sol. in alc. and boiling CCl_4 . The alkali salts of **A** decomp. as do the trichloroacetates (Henry, *Ber.* **12**, 1844 (1879)). **S**. heated the dry Na salt of **A** in a Pt tube in an elec. furnace, the tube being connected with evacuated bulbs. After 3 hrs.' heating, starting at 205° and ending at 340° , the gases in the bulbs were passed through tubes cooled to -15° and -80° , resp. In the latter was obtained a liquid which b. -59° and a liquid which did not dist. at 10° . A gas was evolved, the aq. soln. of which gave a ppt. with Ca and contained trifluoroacetyl fluoride (**I**), b. about -59° , having an irritating odor. **I** reacts violently with alc. and H_2O . The liquid not b. at 10° is **J**. The formation of COF_2 could not be proved—phenylurethan did not result when PhNH_2 in alc. was added. The residue in the Pt tube is NaF and a small amt. of Na_2CO_3 . The most striking property of **A** and its derivs. is their great volatility. A comparative table of b. ps. of the **F** derivs. of AcOH is given as well as a table of the refractive indices of the esters.

H. E. WILLIAMS

Electrochemistry of organic compounds (LOWY) **4**. Action of NO and NH_4OH compounds on Na_3AsO_3 (GUTMANN) **6**. Action of boric acid on mannitol (DUBRISAY) **2**. Action of neutral salts on the rearrangement of acetochloroanilide to *p*-chloroacetanilide (ÄGERLÖF) **2**. Several necessary relations between the physical properties of isomeric organic compounds (KLEMENC) **2**. Acetone and butyl alcohol by fermentation (U. S. pat. 1,437,697) **16**.

Dehydrating alcohol. J. VAN RUYMBEKE. Brit. 184,036, July 15, 1921. In prep. alc. of 98–99% strength, alc. vapors are brought into contact with glycerol which acts as a dehydrating agent. The glycerol preferably flows down a rectifying column up which alc. vapors are passed. A continuous app. is described.

Dehydrating alcohol. J. VAN RUYMBEKE. Brit. 184,129, March 22, 1922. Addition to 184,036 (preceding abstract). A soln. in glycerol of an anhydrous or hygroscopic salt such as CaCl_2 , ZnCl_2 , or K_2CO_3 is used as the dehydrating agent.

Purifying naphthalene. S. P. MILLER. U. S. 1,438,710, Dec. 12. Crude C_{10}H_8 is distd. and the vapors are passed through H_2SO_4 under reduced pressure, at $134\text{--}144^\circ$.

Chlorinating acetylene or other organic compounds. H. H. DOW. U. S. 1,437,636, Dec. 5. C_2H_2 or other org. compds. are chlorinated by alternately bringing Cl into contact with them in the presence of active charcoal or other catalyst and then shutting off the reagents from the catalyst and subjecting the latter to such reduced pressure conditions that all of the products of the resulting reactions will assume the state of vapor, so that they can be distd. and fractionated.

Catalytic oxidation of acenaphthene. G. C. BAILEY and A. F. CRAVER. U. S. 1,439,500, Dec. 19. Acenaphthenequinone, naphthalic acid anhydride or acid and naphthaldehydic acid are prepd. by oxidizing acenaphthene vapor at a temp. of about 400° by the action of air with V oxide on pumice as a catalyst.

Apparatus for production of aldehydes from alcohols. A. A. BACKHAUS. U. S. 1,437,483, Dec. 5. The app. is especially adapted for producing AcH or CH_2O from EtOH or MeOH; it comprises a furnace with a vertical and a horizontal flue for hot gases, a short pipe constituting a catalytic chamber (which may contain a carrier and Cu, Ni, Cr or Fe) removably and vertically mounted in the horizontal flue, a preheater also vertically mounted in the horizontal flue adjacent to the pipe but further from the furnace, a conduit connecting the bottom of the preheater and the catalytic chamber, and a vaporizer connected to the top of the preheater. Vapor of the alc. is supplied from a steam-heated still to the preheater.

Isopropyl alcohol. K. P. McILROY. U. S. 1,438,123, Dec. 5. Gas oil, etc., is gasified to obtain a gas contg. propylene and the latter is hydrated to isopropyl alc. by passing it in contact with a bath of hot dil. H_3PO_4 , H_2SO_4 or NaHSO_4 of progressively decreasing acidity. The isopropyl alc. vapors are removed and condensed. Bu and Am ales. also may be obtained similarly.

Alkyl hydrogen sulfates. FARBENFABRIKEN VORM. F. BAYER & CO. Brit. 185,757, Sept. 8, 1922. Ag or a Ag compd. is employed as a catalyst for the absorption of C_3H_4 or its homolog in H_2SO_4 . Preferably, a substance is added which is capable of forming a froth, scum or emulsion with H_2SO_4 ; e. g., olive oil, castor oil, rape-seed oil, Turkey red oil, CHCl_3 , CCl_4 , tetralin, CS_2 , or stearic acid. The Ag employed may be in a colloidal state or as a salt or complex compd.

Sodium salts of 1,4-anthraquinonedisulfonic acids. C. VERNET and G. RAUCH. U. S. 1,437,571, Dec. 5. Na 1,4-anthraquinonedisulfonate substantially free from the isomeric acids is prepd. by subjecting a mixt. of these acids to the selective solvent action of Na_2SO_4 and NaHSO_4 .

Halogen derivatives of *p*-toluenesulfonic acid, their condensation with amines and transformation into aldehydes. SOC. ANON. POUR L'IND. A BALE. Fr. 483,600, July 31, 1917. The patent covers the prepn. of substances of the type YNRX, in which X = an alkyl, aryl, alkaryl radical or H; Y = an aryl; R = $\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $\text{CH}_2\text{C}_6\text{H}_4\text{ClSO}_3\text{H}$, or $\text{CH}_2\text{C}_6\text{H}_3(\text{SO}_3\text{H})_2$. In an example *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{Na}$ is chlorinated first in the side chain, then in the nucleus. The product is condensed with PhNHEt or is oxidized with $\text{Na}_2\text{Cr}_2\text{O}_7$ to $\text{HO}_2\text{SC}_6\text{H}_4\text{ClCHO}$.

***L*-Glucosan.** A. PIETER. U. S. 1,437,615, Dec. 5. Polysaccharides such as sawdust, cotton or starch having mol. wts. greater than those of the trisaccharides are utilized as sources of *L*-glucosan by subjecting them to dry distn. under a pressure of 12-30 mm. Hg at temps. of 200-300°.

Tri-*o*-tolylguanidine. R. V. HEUSER. U. S. 1,437,419, Dec. 5. Tri-*o*-tolylguanidine is prepd. by reaction on di-*o*-tolylthiourea with *o*-toluidine and Pb oxide, with such an excess of *o*-toluidine above the theoretical amt. that it serves as a thinner to permit completion of the reaction.

Methyl *o*-menthoxybenzoate. G. BLIEBERGER. Can. 226,478, Nov. 21, 1922. About 100 parts by wt. of *o*- $\text{HOOC}_6\text{H}_4\text{CO}_2\text{Me}$ is heated in an inert atm. under slight pressure with 80 parts of menthol. The forerunner is collected and the combined reaction mass distd.

Benzyl succinate. M. BYE and L. H. CARLSON. U. S. 1,439,605, Dec. 19. Benzyl succinate in the form of a cryst. powder is obtained by heating succinic acid with benzyl alc., filtering, adding a solvent such as alc. and then freezing and drying.

Polymerizing diolefins as they are formed. H. PLAUSON. U. S. 1,436,819, Nov. 28. Diolefins at the time of their formation are polymerized by increasing the temp. or pressure or by prolonging the time of the reaction. A mixt. of equal vols. of C_3H_4 and C_3H_6 may be used to form 1,3-butadiene by passing the mixt. under pressure through a steel tube heated to 350-400°, the 1,3-butadiene being liquefied and sepd. as formed and the unchanged gases returned to the reaction tube. By carrying out the same reaction with addn. of C_4H_6 vapor and alkali in an autoclave and permitting the pressure to rise to 55-65 atm. a considerable amt. of a rubber-like product is obtained. Allylene and C_2H_4 and C_3H_2 and propylene also may be used to prepare diolefin hydrocarbons.

Chlorinated hydrocarbons. GLYSYN CORPORATION. Brit. 168,676, Feb. 18, 1921. Propylene chloride, or a similar compd. obtained by satg. an unsatd. hydrocarbon with Cl_2 is further chlorinated in the presence of a gaseous or vaporized S compd. such as SO_2 , S chlorides, or sulfuryl chloride. Trichlorohydrin is thus obtained. The S compd. should not exceed 1% of the amt. of Cl_2 . SO_2 and Cl_2 may either be introduced separately

into the chlorination vessel or be previously mixed. The reaction may be effected in actinic light such as direct sunlight, ultra-violet light, or the light of a flaming arc, and at atm. or higher temps. The product is sepd. by distn. from any unchanged propylene chloride.

Tetra-substituted ureas. A. P. TANBERG. U. S. 1,437,027, Nov. 28. Dimethyldiphenylurea is produced by treating with COCl_2 about equi-mol. proportions of PhNHMe and PhNMe_2 dissolved in C_6H_6 or an equiv. solvent at a temp. of about 60° . After distn. of the solvent from the reaction products, the residue is treated with dil. HCl to remove PhNMe_2 and leave the dimethyldiphenylurea, which is purified by subsequent washing and crystn. The reaction may be generally applied to secondary aromatic amines treated in soln. with COCl_2 in the presence of a tertiary amine or other non-interfering basic compd. which will combine with the HCl set free to form a product which is non-reactive with the desired substituted urea.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

Behavior of several cyclic compounds in the human and animal organism. E. SCHEMPF. *Z. physiol. Chem.* 117, 41-7(1921).—Phenylacetic acid is excreted by the cat as phenaceturic acid. The result of Totani (*C. A.* 5, 1621) that the hen excretes phenylacetic acid as phenacetornithuric acid was not confirmed completely. The m. p. and $[\alpha]_D$ of the product were different than reported. *o*-Nitrophenylacetic acid was excreted by the dog and by man unchanged (57% and 74%, resp.). The para compd. gave 19% and 31% recovery. Phenylbromoacetic acid appeared as inactive mandelic acid in the dog and man (40% and 52%, resp.). Of α -thiophenic acid administered to the dog 28% reappeared as thiophenuric acid; in man 71% appeared as this compd. When pyromucic acid was administered to man 71% was recovered as pyromucuric acid.

R. L. STEHLÉ

Nature and origin of diastatic enzymes. E. ROTHLIN. *Münch. med. Wochschr.* 68, 1393-5(1921); cf. *C. A.* 16, 3908; 17, 290.—Biedermann asserted that certain ions or combinations of ions are able to give origin to diastase; in an enzyme-free amylose soln. later the origin of diastase under such conditions was attributed to zymogen adhering to the starch. It is shown that such zymogen would have to be resistant to heat and it is probable that Biedermann's autolysis of amylose is due to bacterial infection. The proof is indirect. Reply by BIEDERMANN. *Ibid* 1428.

S. AMBERG

Carmelo Ciaccio. ANON. *Biochim. terap. sper.* 9, 221-5(1922). H. W. B., 3RD. **Osmotic resistance and phosphatides of the blood. New quantitative methods.** R. BRINKMAN. *Arch. néerland. physiol.* 6, 451-516(1922).—Previous investigations have furnished little evidence concerning the chem. compn. of the membrane surrounding the red blood cells, except the indefinite statement that "lipoids" play some role. B. has cleared up a good deal of this mystery by extensive expts. The first step towards an exact investigation is the use of an "equilibrated" salt soln., e. g., a soln. which at any concn. keeps up the same colloidal state of the membrane of the cells. A pure NaCl soln. cannot be considered as appropriate as it exerts a lyotropic influence on the colloids, which varies according to the concn. of the soln. If pure NaCl solns. of various concns. are tested on the blood cells the mere osmotic influence and the lyotropic one are mixed in an uncontrollable manner; the curve obtained, when measuring the pro-

gressive percentage of blood cells hemolysed by pure NaCl, is not a true picture of the real osmotic resistance. The variable lyotropic influence of NaCl is counterbalanced by keeping the concn. of H^+ and of Ca^{++} const. This is done by introducing the buffer system $H_2CO_3 + NaHCO_3$ which according to the equations $H^+ = K \cdot (H_2CO_3 / HCO_3^-)$ and $Ca^{++} = K^1 \cdot (H^+ / HCO_3^-)$ fixes the concn. of both ions, independent of the total concn.; the CO_2 tension must be kept const. by using tubes which are well closed and filled to the top and by pouring paraffin oil on the solns. The undil. soln. is composed of: 0.7 % NaCl, 0.2 % $NaHCO_3$, 0.01 % KCl, 0.02 % $CaCl_2 \cdot 6H_2O$, and CO_2 in such a quantity that $[H^+] = 0.45 \cdot 10^{-7}$. The conditions of keeping H^+ const. as well as Ca^{++} are described by Rona and Takahashi (*C. A.* 7, 2232). If the osmotic resistance is detd. with this soln. it is found that about 80 % of all red blood cells have the same osmotic resistance, 10% are decidedly less resistant, e. g., "old" cells, and 10% are very much more resistant, e. g., "young" cells. If the red blood cells are washed in the soln. described an increase of the resistance is obtained which is due to a washing off of hemolysing lipoids (phosphatides), taken up by the blood cells from the plasma by adsorption on the surface. The curve of osmotic resistance (concn.: hemolysed percentage) of the washed blood cells represents the real osmotic resistance free from the hemolysing lipoids of the plasma; the washed cells behave like the "young" or regenerated cells. To obtain blood cells with a high tendency to dissolve the normal ratio cholesterol: lecithin is changed by expt., by injecting lecithin into a rabbit fed on a diet free from cholesterol. On the other hand by injecting cholesterol, the osmotic resistance is increased. This decrease (or increase) is observed with the unwashed cells only, as one should expect from B.'s theory, viz., only the surface layer of cells is changed by these injections. The resistance of the blood cells can be decreased, also, by passing the blood through the spleen; in this case, also, the decrease is observed if the cells are not washed. Referring to a previous work by Hamburger (*C. A.* 16, 1983), B. also suggests the use of a mixt. of primary and secondary phosphates (having the same pH) instead of the NaCl soln. described. This soln. is dild. according to a geometric progression. In order to exam. more closely the importance of the lipoids, B. exts. the phosphatides and the cholesterol one after the other according to the method prescribed by Bang (*C. A.* 13, 2226, 2228). (1) With gasoline and (2) with alc. Both fractions of the extd. lipoids are suspended again in salt soln., any formation of foam being avoided. It is found that the fraction which contains more phosphatides has a hemolytic action; this is not the case in the fraction contg. cholesterol. A simple method is worked out for clinical use which makes it possible to study with 3 cc. of blood the hemolytic activity of the phosphatides present and the inhibition of this activity by cholesterol. Extensive expts. on animals producing hemolysis by injecting phosphatides are described. In an extended exptl. intoxication of that kind the formation of megalocytes was observed. The expts. prove that the surface of the blood cells contains lecithin and cholesterol in a variable proportion.

R. BEUTNER

The origin and the nature of thrombin. P. NOLF. *Arch. néerland. physiol.* 7, 348-51 (1922).--An emulsion of blood platelets or leucocytes, carefully washed in isotonic oxalated salt soln., does not coagulate, *per se*, a pure soln. of fibrinogen contg. Ca. The coagulation only takes place if a trace of plasma or of serum is added. Neither plasma nor serum alone is active. It is possible to isolate in a pure state the coagulant substance from the plasma; if oxalated horse serum is left standing at 0° for some days it settles down as a ppt. N. calls this substance *thrombocyme*; it is found to be very active in coagulating plasma in the presence of blood platelets or leucocytes. If oxalated plasma of a dog, after the addn. of Ca again, is shaken with an excess of $CHCl_3$ it coagulates instantly. The serum sepd. from this coagulate coagulates a dil. oxalated soln. of fibrinogen, and, also, the plasma of birds which otherwise is very stable. This coagulating action of the

serum disappears after some days; a proteolytic action is then observed if the serum is mixed with a fibrinogen soln. The plasma of birds is also coagulated after standing. N. concludes that the plasma contains 2 kinds of proteins: (1) the "thrombocytes," originating from the white blood cells and the extra-hepatic endothelial cells and (2) fibrinogen, thrombogen, antithrombosin and antithrombolyisin, secreted by the liver.

R. BEUTNER

Observations relating to the radiation of potassium salts, and on the question whether cesium is also radioactive. W. E. RINGER. *Arch. néerland. physiol.* 7, 431-40(1922).—Referring to the well known radio-physiol. investigations of Zwaardemaker, R. states that com. preps. of Cs salts are radioactive but that by producing a ppt. of $\text{Fe}(\text{OH})_3$, CuS or BaSO_4 in solns. of these salts the radioactive impurity is removed. *Cs as such is not radioactive.* This is not favorable to Zwaardemaker's theory that Cs can replace K in physiol. salt solns.; it seems doubtful, therefore, whether the physiol. action of K is due to its radioactivity.

R. BEUTNER

Why is the danger of drowning greater in salt water than in fresh water? The resorption of fresh, brackish and sea water in the lungs. ERNST LAQUEUR. Pharmacol. Instit. Univ., Amsterdam. *Arch. néerland. physiol.* 7, 441-9(1922).—Equal quantities of distd., fresh, brackish and sea waters were injected per trachea in the lungs of rabbits. After 15 min. the animals were killed and the quantities of water contd. in the lungs detd. It is found that resorption is the more complete the less the NaCl content of the injected liquid. Also, the Cl content of the liquid injected was detd. The slower resorption of sea water causes the greater probability of drowning in the sea.

R. BEUTNER

The threshold value of acid taste. G. LILJESTRAND. *Arch. néerland. physiol.* 7, 532-7(1922).—*Acid taste is not due to any definite p_H but rather to the titration capacity of the soln.* Comparing, at first, the acid taste of various pure acids, *e. g.*, detg. the smallest concn. which has a slight acid taste, it is found that the strong mineral acids *taste acid* at a $p_H = 3.4$ to 3.5, the weaker org. acids like acetic, lactic, citric and butyric, at $p_H = 3.7$ to 3.9. Quite different results are obtained, however, if some of the well known buffer-salt solns. are used. If such a mixt. is prepd., having a $p_H = 3.9$, it tastes much more acid than a pure acid of equal p_H and besides the acid taste is kept up for a long time in the mouth while with pure acids it disappears rapidly. If a buffer mixt. of the minimal p_H which just gives an acid taste is prepd. the p_H is found to be: 5.6 for a mixt. of AcOH and AcONa , or 6.3 for the mixt. of citrate and NaOH , according to Sørensen. This proves that a soln. of a large titration capacity, as, *e. g.*, the buffer mixts., may produce an acid taste at a p_H scarcely different from the neutral point.

R. BEUTNER

Sensation and reaction in protoplasm. Bathmotropism and inotropism in the heart. J. DEMOOR. *Bull. acad. roy. med. Belg.* [5] 2, 500-13(1922).—Many older investigations are cited to prove that the process of *sensation* and of *reaction*, due to irritation, are independent of each other although related in the organism. "Sensation" is the direct physico-chem. consequence of the action of the irritation. "Reaction" is the transformation of energy, producing profound changes in the chem. equil. of the organ. Sensation is not subject to fatigue; such is only the case with the processes of reaction. Expts. on the influence of adrenaline on the isolated rabbit heart are described; it is possible to discriminate 3 different, independent actions, some of which can be suppressed by previously administrating glucose. It is evident that the excitability (sensation) and the contractibility (reaction) of the muscle fibre are independent. By adding glucose the contractibility alone is influenced. This is due to an influence on metabolic processes which restore the chem. equil. disturbed by the contraction.

R. BEUTNER

Odor and its relation to molecular structure. R. DELANGE. *Bull. soc. chim.* **31**, 589-630; *Rev. sci.* **60**, 505-43(1922).—Odoriferous compds. show evidence of the existence of partial valence and residual affinity in the mol. O is considered tetravalent. In non-odoriferous sp. compds. the valences are mutually neutralized. C. discusses the classification and measurement of odors and the relation between odor, chem. constitution, and phys. properties.

JAMES A. BRADLEY

Note on the inhibitory effect of urine on the precipitation of urea by nitric acid. E. A. WERNER. *Chem. News* **125**, 100-1(1922).—Urine of a known urea content permitted the pptn. of only 44.8% of the total urea as nitrate. An aq. soln. of the same concn. gave a pptn. yield of 77.73%. The inhibitory effect is ascribed to colloids.

JAMES A. BRADLEY

The kinetics of the coagulation of protein by heat. HEINRICH LÜERS AND MAX LANDAUER. *Z. angew. Chem.* **35**, 469-71(1922).—The process consists of two stages: (a) a chem. denaturation of the protein, and, (b) the actual coagulation which is a colloid phenomenon. The denaturation of leucosin was found to be a monomol. reaction with a temp. coeff. of 1.47 per degree.

JAMES A. BRADLEY

The course of oxidation processes. HEINRICH WIELAND. *Ber.* **55B**, 3639-48 (1922).—W. discusses the theory that cell oxidations are brought about by a change of the O by an enzyme into a specially reactive, peroxidic form. In reductions the H is activated. Numerous examples are cited to demonstrate the theory. J. B. BROWN

Studies on enzyme action. XXI. Banana gel and banana sucrase. K. GRO. FALK AND GRACE MCGUIRE. *J. Biol. Chem.* **54**, 655-69(1922); cf. *C. A.* **16**, 3511.—Exts. of banana pulp made with 0.14 to 0.67 *M* NaCl formed gels when dialyzed against tap water. The higher concns. of NaCl were employed with large vols. and the gels were soft but, up to a concn. of 0.57 *M* NaCl, the gel contained all the sucrase. The Ca in the tap water appeared to be responsible for the gel formation. Exts. were made, at p_H 5.0, with NaCl, NaNO₃, Na₂SO₄ and MgSO₄ solns. of different concns.; these were dialyzed and tested for gel formation after addn. of CaCl₂ and NH₄OH to p_H 7.0. In each case, with the possible exception of Na₂SO₄, increasing concn. of salt in the extg. liquid impaired the gel-forming properties of the dialyzed ext. The max. sucrase extn. was obtained with concns. of NaCl between *M* and 2*M*, of NaNO₃ of about 0.24 *M*, of Na₂SO₄ of 0.2 *M* and of MgSO₄ of 0.24 *M*. This difference in gel-forming and sucrase extn. indicates that the 2 properties are not due to the same substance. Boiling the exts. destroyed both the gel-forming substance and the sucrase. Pancreatin formed gels in the unboiled exts. and the filtrates from these gave no additional gel on dialysis or subsequent treatment with CaCl₂ and NH₄OH. Boiled pulp filtrates did not form gels with pancreatin; neither did boiled pancreatin solns. form gels with pulp filtrate. The pancreatin did not contain sucrase. An ext. made with 0.25 *M* NaCl, with HCl added to a reaction of p_H 3.5, yielded a filtrate in which, after 6 days a gel sepd. Gels dialyzed against distd. H₂O liquefied and gave slightly cloudy filtrates which contained sucrase. If centrifuged at 35,000 r. p. m. for 7 min., before filtering, the filtrate was more active than if not so treated.

I. GREENWALD

A series of metallo-cysteine derivatives. I. L. J. HARRIS. *Biochem. J.* **16**, 739-46(1922).—The violet coloration obtained when NH₃ is added to cysteine is shown to be due, also, to the presence of traces of a metallic (generally ferric) salt; in the complete absence of the latter no color is developed. The theory developed is as follows: Cysteine is an acid, and in the presence of ferric ions, and in an alk. soln., it forms a violet-colored ferric derivative. The main characteristic of cysteine is its reducing power: $2 \text{ COOH}-\text{CHNH}_2\text{CH}_2\text{S} \xrightarrow{[\text{H}+\text{O}]} (\text{COOH}\cdot\text{CHNH}_2-\text{CH}_2\text{S}-)$, + H₂O. If excess be present and the supply of air be limited the cysteine is oxidized to cystine at the expense of the ferric ion, which is reduced to the ferrous state. The

latter yields no colored derivs. with cysteine and the soln. therefore fades. If air be blown through the system, the Fe is oxidized, and if unoxidized cysteine remains, the violet color will again be developed. Mn, Cu and Hg act similarly to Fe. B. H.

Lactase studies. E. FREUDENBERG AND P. HOFFMAN. *Klin. Wochschr.* **1**, 2333-4 (1922).—Lactase isolated from the intestine of a calf or an infant shows an optimum activity at a p_H of 5.0. The activity of calf lactase is enhanced by the presence of phosphate; the activity of infant lactase is retarded by phosphate. Calf lactase hydrolyzes lactose quantitatively in cow milk whey, but the hydrolysis is only partial in human milk whey. The difference in action can be accounted for by the fact that calf milk whey contains more PO_4 than human milk whey. Distressing bacterial fermentations occur more frequently in infants after the ingestion of cow milk than after the ingestion of human milk because the lactose is not readily hydrolyzed and hence not absorbed when cow milk is fed which leads to a bacterial fermentation in the lower intestine.

MILTON HANKE

Glutathione. II. A thermostable oxidation-reduction system. F. G. HOPKINS AND M. DIXON. *J. Biol. Chem.* **54**, 527-63(1922); cf. *C. A.* **15**, 3119.—“When a tissue is washed until it has lost its power of reducing methylene blue the subsequent addn. of glutathione (a dipeptide of glutamic acid and cysteine) to a buffer soln. in which the tissue residue is suspended restores reducing power. This is the case when the dipeptide is added in its oxidized (disulfide) form. The tissue residue first reduces the S group and a system is thus established which under anaerobic conditions continuously reduces methylene blue until an equil. is reached. A tissue, washed until it no longer ‘respires’, will, when suitably treated and supplied with glutathione, again take up O_2 and yield CO_2 . Such part of its reducing and respiratory activity as is regained by a washed tissue on the restoration of glutathione remains almost unaffected when the tissue is heated to 100° or even thoroughly extd. with boiling H_2O . The residue from muscular tissue so heated and extd. will in the presence of glutathione take up about 400 cu. mm. of O_2 per g. of dry material. During the earlier stages of O_2 uptake the quotient CO_2/O_2 is usually about unity; later it falls to lower values. Glutathione does not appear to be a coagent in any known enzymic system. The facts suggest that coexisting in living tissues with the specialized enzymic mechanisms is a thermostable mechanism for oxidations and reductions. Materials in some close association with structural elements are oxidized, anaerobically and aerobically, with the coagency of the S group in glutathione.”

A. P. LOTHROP

The combined uric acid in beef blood. ALICE R. DAVIS, ELEANOR B. NEWTON AND S. R. BENEDICT. *J. Biol. Chem.* **54**, 595-9(1922); cf. *C. A.* **16**, 1801 and *C. A.* **9**, 1634.—The combined uric acid compd. in beef blood is made up of 1 mol. of uric acid and 1 mol. of *d*-ribose minus 1 mol. of H_2O . The compd. crystallizes in typical colorless square plates, very difficultly sol. in cold H_2O but dissolving in boiling H_2O and in alkali. It is insol. in alc. and Et_2O . The soln. is acid in reaction and, if not too dil., is very apt to form a water-clear gel. The compd. is not pptd. by Ag-Mg mixt. and gives no reduction with alk. Cu solns. As compared with pure uric acid it gives a relatively small amt. of color with phosphotungstic acid. It is apparently a monobasic acid; $[\alpha]_D^{20}$ of the Na salt 20.42° . It does not contain H_2O of crystn. and does not melt up to 300° . The *d*-ribose was identified by its angle of rotation and its phenylosazone. The yield is about 0.6 g. from 15 l. of blood.

A. P. LOTHROP

Pigments of the Mendelian color types in maize: isoquercitrin from brown-husked maize. CHAS. E. SANDO AND H. H. BARTLETT. *J. Biol. Chem.* **54**, 629-45(1922).—“A series of color types in maize involving pigments of the flavonol and anthocyanidin groups has been genetically analyzed by Emerson. The known genetic constitution of these color types makes it very desirable to conduct parallel chem. investigations

with them in order to understand the operation of the Mendelian factors involved. As a beginning in this work a flavonol glucoside has been isolated from brown-husked maize, one member of Emerson's series and the lowest one showing the presence of a pigment of the groups under consideration. This glucoside is found to be the same as Perkin's isoquercitrin, originally isolated from cotton, and probably the same as an unnamed glucoside isolated by Heyl from pollen of ragweed. It is a monoglucoside yielding only glucose and quercetrin on hydrolysis." The extn. of the material is very tedious and the yield amounts to 0.4% of the air-dried maize used. The product forms a felty mass of primrose-yellow needle-like crystals; m. 220–222.5°; gives an olive-green color with FeCl_3 , an intensified yellow color on addition of Na_2CO_3 or dil. NH_4OH , a yellow ppt. with $(\text{AcO})_2\text{Pb}$, and a pale rose-red color when reduced with Mg and HCl; recrystd. from boiling H_2O it contains one mol. of H_2O of crystn.; it is sol. in AcOEt . The spectral transmission of the substance throughout the visible spectrum and ultra-violet is given and the suggestion is made "that spectrophotometric and spectrographic comparison of the pigments of the flavones, flavonols, and anthocyanidins may possibly afford the best evidence as to the points of attachment of the sugar residues in the glucosides, since the removal of a particular OH group by condensation with sugar might be expected to give a glucoside with approx. the same transmission as the non-glucoside with a H instead of a OH in the same position." A. P. LOTHROP

Experiments on cellular permeability. Permeability of the cornea of the living eye. W. MESTREZAT, PIERRE GIRARD AND V. MORAX. *Compt. rend. soc. biol.* **87**, 144–7 (1922).—The cornea is a double cellular membrane and lends itself for the exptl. study of permeability *in vivo*. This was done by enclosing the eye of a rabbit (previously treated with novocaine) in a special glass bulb fitting well into the orbit and filling the bulb with the test solns. After exposure for 30 min. the eye was carefully washed and the contents of the anterior chamber were removed with a fine needle for analysis. The other eye served as the control. $\text{Ca}(\text{NO}_3)_2$ and MgSO_4 were used. The anions and cations of these salts do not penetrate through the cornea in equiv. amts. Thus, 2 ions of (NO_3) go with 0.03 to 0.54 ions of Ca; 1 ion of (SO_4) for every 0.38–0.65 ions of Mg. The acidity of the medium may increase the permeability but it does not change the proportion of the ions. S. MORGULIS

The permeability of cells to ions. The permeability of the cornea and the selective ionic permeability. W. MESTREZAT, PIERRE GIRARD AND V. MORAX. *Compt. rend. soc. biol.* **87**, 227–30 (1922).—The authors injected into the anterior chamber of the eye of rabbits and dogs (treated previously with novocaine) $\text{Ca}(\text{NO}_3)_2$ and MgSO_4 solns. made isotonic with aqueous humor through the addn. of NaCl or sucrose. Before the substance was injected a similar quantity was withdrawn from the anterior chamber; 30 to 45 min. later a sample of the fluid was again withdrawn from the anterior chamber and analyzed for the cations and anions injected. The results revealed invariably a great alteration in the concn. of both ions which however was not proportional, thus showing that the anions and the cations are differentially absorbed. When similar expts. were made on enucleated eyes the compn. of the injected salts was found to remain without change in the anterior chamber. This is considered by the authors as conclusive proof that there is selective permeability for different ions, and that this is associated with an actual resorption through the blood. S. MORGULIS

Diurnal variation in the hydrogen ion concentration of littoral sea water. R. LEGENDRE. *Compt. rend.* **175**, 773–6 (1922).—Hourly samples of sea water at Comcarneau were taken on Sept. 15 from 7 hr. to 19 hr. (7 A.M. to 6 P.M.). High tide occurred at 10 hr. 36 min., low tide at 17 hr. 2 min. The sea was calm, sun generally visible, sky partly cloudy, and the barometer rose from 760.7 to 766.7 during the observations. The temp. at 7 hr. was 13.6°; it rose to 14.6° at 16 hr. and fell to 14.2° at 19 hr. Sp.

gr. at 7 hr. 1026.3, at 19 hr., 1026.0 at other hrs. between these figures: O dissolved in mg. per l. at 7 hr. was 7.9 which increased up to 9.9 at 16 hr. and fell to 7.2 at 19 hr. p_{H} values were quite parallel to O dissolved, being 8.0 at 7 hr., rising to 8.19 at 15 and 16 hr., then falling to 8.01 at 19 hr. The diurnal variation in the O content is ascribed to the photosynthesis of plankton and other algae whereby the consumption of CO_2 diminishes the concn. of the H ions, and at the same time O is set free. L. W. RIGGS

Mechanism of hemolysis and of agglutination by ions. F. HÄFFNER. *Arch. ges. Physiol.* (Pflüger's) 196, 15-59 (1922).—The lysis and agglutination of red blood cells as a result of exposure to a series of electrolytes—acids, alkalies, metallic salts, dyestuffs—were detd. Electrolytes with an active anion, as also those with an active cation, showed a considerable degree of uniformity in their action, inasmuch as in moderate concns. they were lytic and in high concns. (under certain conditions) they were fixing and at the same time agglutinating. The activities of anions and of cations were sharply differentiated in that the fixative action of the cations was increased by augmentation in the OH concn., and the effect of the anions was intensified by increase in the H^+ concn. Certain cations were characterized by an agglutinative action without lysis in the lower concns. The type of reaction produced by particular ions was related to the nature of the metallic salt used in that the lytic action increased, in relation to the fixing property, the more noble the metal. Agglutination of cells by electrolytes may, or may not, be associated with fixation. When agglutination without fixation occurs, as with cations in low concns., the reaction consists in a flocculation of the stromata. While salts of the trivalent metals are flocculating in a physiol. saline soln., other cations, as H^+ , Hg^{++} , cause the flocculation of erythrocyte stromata only in a medium poor in electrolytes. Thus under certain conditions NaCl and other neutral salts are inhibitory. The flocculation reaction consists in an actual pptn. of the stroma substance of each individual cell, as can be demonstrated microscopically or by observing the increased resistance of the cells when exposed to lytic agents. When the reaction between cell and electrolyte involves both a fixation and an agglutination, such as is induced by high concns. of ions, it is accompanied by a lysis of the cells, that is, an alteration in the hemoglobin, involving the formation of hemoglobin-cation-anion complexes. With the disruption of the hemoglobin mol. through union with an ion the cation complex shows the color and spectrum of the brown hematin, the anion complex the color and spectrum of the red compd. G. H. S.

Studies on the nature of the Abderhalden reaction. VIII. Experiences with different methods. Comparative estimation of the serum nitrogen. E. ABDERHALDEN. *Fermentforschung* 6, 230-7 (1922); cf. C. A. 16, 3970.—When the reaction is positive with solid substrate covered with serum, the amt. of N in the serum increases, while with a negative reaction the amt. of N in the serum is unchanged or reduced. This is evidence that there is digestion of the substrate and not alone of the serum, in positive Abderhalden reactions, contrary to the opinion that has often been expressed. It does not decide whether or not the serum is also digested. Of the different methods employed in applying the Abderhalden reaction (N detn., interferometer or capillarity measurements, direct observation of turbidity when serum acts on substrate), all give concordant results except the last, which should be discarded for accurate work. IX. E. ABDERHALDEN and E. WERTHEIMER. *Ibid* 263-8.—Expts. to det. the place where the so-called protective enzymes are formed, showed that thyroidectomized animals do not form enzymes digesting thyroid after injection of thyroid tissue. Likewise castrated animals do not form enzymes digesting testicle substance after injection of this material. On the other hand, castrated animals give a positive Abderhalden reaction to liver tissue after being injected with liver tissue. These results were interpreted to mean that the enzymes which cause the Abderhalden reaction are preformed in the tissues

and in the same cells that serve as substrate. If the body lacks a definite organ it cannot discharge into the blood enzymes capable of digesting this sp. tissue. H. G. WELLS

The chemical dynamics of carbohydrate digestion in the mammalian duodenum. C. BÖHNE. *Fermentforschung* 6, 200-29(1922).—This is a study of the diastatic action of a glycerol ext. of beef and sheep pancreas under the influence of various electrolytes present in pancreatic juice, the H-ion concn. being always known. Three factors were found to be of importance. (1) The anions of the diastase-salt complexes (Cl^- , HCO_3^- , H_2PO_4^- , HPO_4^{--}) first transform the inactive resting prozyme into the active enzyme. (2) The existing H-ion concn. regulates essentially the course of the digestion process, so that apparently the selective influence of the anions of the coenzymes remains limited to the activation of the enzyme. (3) The influence of the concn. of the added salt soln. is less important although noticeable when this concn. varies greatly even if the H-ion concn. is not much altered. The reaction of the duodenal contents corresponds closely with the optimal condition for the phosphate-carbonate-diastase, (p_H 6.6-7.1). Pancreatic juice contains only about $1/4$ as much NaCl as the intestinal juice, the deficit being made up to a desirable concn. by the neutralization of the gastric juice, for with too high a concn. of NaCl the diastatic activity is reduced. Apparently the stepwise hydrolysis of starch through maltase and saccharase is to avoid flooding of the organism too rapidly with glucose. Protection against too rapid cleavage of proteins and fats is provided by the reaction of the duodenal content (6.6-7.1) which is not the optimal p_H for either trypsin or lipase. H. G. WELLS

Correction and addition to eighth report on enzyme action. Isolation of enzymes from yeast protein. The activity of the sols as a function of the colloid state. A. FODOR. *Fermentforschung* 6, 238(1922); cf. *C. A.* 16, 2885.—The error was made of reckoning the P content of yeast phosphoproteins as P_2O_5 but expressing it as P. Therefore the figure 3.98% P should read 1.74% P. The different fractions of protein pptd. from yeast maceration fluids by increasing acid concn. show no considerable differences in chem. compn. although varying in their colloidal properties. H. G. WELLS

Studies on proteolytic and peptolytic enzymes. E. ABDERHALDEN AND A. FODOR. *Fermentforschung* 6, 248-62(1922).—An investigation to det. whether pepsin and trypsin themselves attack peptones and polypeptides. As preps. were found which digested proteins and not peptones it is believed that the demonstration of the independence of proteases and peptases is made. If a mixt. of casein and pepsin is treated with a trypsin soln. which does not digest peptone alone, a rapid hydrolysis of peptone occurs, suggesting that the casein and pepsin do not exist indifferently together in a soln., but there must be some relation or combination, whether chem. or phys. Evidence is obtained that in the digestion of casein there occurs, as a distinct step, the splitting out of P, which is considered evidence of the existence of a protein-phosphatase. H. G. WELLS

Synthesis of carbohydrates and proteins (THATCHER) 10. Constitution of the bile acids (BORSCHET, HALLWASZ) 10. Unsaturated bile acids (BOEDCKER, VOLK) 10. Melanin formation from organic substances (ADLER, WIECHOWSKI) 10. Importance of impurities (ALEXANDER) 2.

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

A rapid clinical method for the determination of the reducing substance in the cerebrospinal fluid: the methylene-blue method. M. KASHAHARA AND S. HATTORI. *Am. J. Diseases Children* 22, 218-9(1921).—To 1 cc. 0.004% methylene-blue soln. (Methylene blue f. Bac. Gruebler) 3 drops 10% KOH is added. Cerebrospinal fluid is

added from a buret until the soln. becomes perfectly colorless on boiling. The % of reducing substance, glucose, is equal to 0.01 divided by the no. of cc. spinal fluid used.

S. AMBERG

Determination of blood. J. GATTNER AND E. SCHLESINGER. *Deut. med. Wochschr.* 48, 522-3(1922).—The benzidine reaction for blood is utilized for detn. of occult blood in the feces in the sense that under the conditions of a uniform technic changes in the amt. of occult blood from day to day can be detd.

S. AMBERG

The hemoglobin determinations according to Sahli and Autenrieth-Königsberger. E. KOMIYA AND T. KATAKURA. *Deut. med. Wochschr.* 48, 591-2(1922).—To avoid errors it is recommended to let the blood-HCl mixt. stand for 10 min. at a temp. of 30-60°. The detns. made according to the original procedure may vary very much because the mixts. become darker, depending on the lapse of time.

S. AMBERG

The clinical significance of blood sugar. H. SCHIROKAUER. *Deut. med. Wochschr.* 48, 1034(1922).—In contra-distinction to Offenbacher and Hahn, who demand that blood sugar should be detd. only in whole blood, it is stated that the sugar should be detd. in serum, or in whole blood and serum.

S. AMBERG

Alizarin staining of urine sediments as a diagnostic method in internal medicine (and remarks with regard to the calcium titration). E. FRIEDLÄNDER. *Deut. med. Wochschr.* 48, 1035-6(1922).—A drop of Na alizarinsulfonate 1% aq. soln. is mixed on the slide with a drop of urine sediment by means of the edge of the coverglass. After one minute, the slide is examd. Normally brick-red platelets are pptd.; this ppt. is wanting or is replaced by a little finely granular ppt. in acute and chronic nephritis, croupous pneumonia and the majority of pyelitis and cysto-pyelitis but not in uncomplicated cystitis. On dissolving the platelets with AcOH a network of a mucin-like substance is seen. Negative urines showed a much diminished CaO content. On ashing of urines, careful neutralization, very slight acidification and filling up to original vol. with water, the alizarin test is the same as with the urine itself. Normal urines, diltd. so that their CaO and P₂O₅ concns. fall below those necessary in solns. of Ca acetate and CaCl₂ with NaH₂PO₄ and Na₂HPO₄ for the pptn. of platelets, still give a few on addition of alizarin. Addition of Ca to negative urines up to 0.01% CaO makes the reaction positive. Urine with otherwise normal amts. of mineral constituents react with a content of 0.003% CaO. This shows that in the pathological urine the other mineral constituents are diminished. The CaO was detd. by the KMnO₄ titration method with N/140-N/150 KMnO₄; it is particularly emphasized that such dil. solns. give very good end-points.

S. AMBERG

Estimation of urobilin. L. PINCUSSEN. *Deut. med. Wochschr.* 48, 1074-5(1922).—By addition of Lugol soln. to urine all urobilinogen is transformed into urobilin. Ten cc. of this urine is taken and 10 cc. satd. Zn acetate soln. is added; it is well mixed and filtered. The filtrate is compared with regard to its fluorescence with fluorescein solns. starting with 1:1000 and dilg. this soln. 1/2, 1/4, etc., in the usual manner. The corked tubes keep well when protected against light. About 0.01 mg. urobilin in 10 cc. can be recognized.

S. AMBERG

Estimation of urobilin. A. ADLER. *Deut. med. Wochschr.* 48, 1442-3(1922).—Polemical against Pincussen (preceding abstract).

S. AMBERG

A simple, quick and accurate method for the determination of blood sugar with two drops of blood. R. WEISS. *Münch. med. Wochschr.* 68, 1255-61(1921).—Weiss reported a very simple blood sugar method, using Pavy soln. A little app. has been devised for this purpose. With an accurate pipet 0.1 cc. blood is placed in a small test tube, contg. a few cc. abs. alc. The mixt. is left standing 1/2 hour under frequent shaking. Then it is filtered through a small hardened filter, with frequent renewal

of alc., into a small flask. The alc. is evapd. and 0.3 cc. each of Pavy i and ii and 1.8 cc. distd. water are added. The stopper is placed in position holding a glass tube and a glass rod. The contents are brought to gentle boiling, the flask just touching the asbestos wire net. As soon as the fluid begins to boil the glass rod is replaced by a buret contg. 0.01 *N* glucose soln. This soln. is added drop by drop into the boiling fluid. After each drop the bottle is shaken. When the soln. is completely decolorized the amt. of glucose added is read. 0.3 cc. Pavy requires 0.0003 g. glucose. The 0.01 *N* glucose keeps only for a short time, so that its titer has to be detd. in exactly the same manner. A series of comparisons of the micro and the macro titration with Pavy is given.

S. AMBERG

Further observations on the cobalt nitrite reaction for potassium in animal and vegetable cells. A. B. MACALLUM. *Arch. néerland physiol.* 7, 304-8(1922).—Co nitrite in a properly prepd. soln. is an extremely sensitive reagent for K in animal and vegetable cells; it is far from being as sensitive a precipitant for NH_4 ; if NH_4 salts are present in tissues they can, by the addn. of CH_3O to the reagent, be converted into hexamethylenetetramine which does not form a ppt. with the reagent. Creatine is also pptd. by the reagent; creatinine, guanidine, and arginine are not pptd. Pptn. of creatine is not prevented by adding CH_3O . The reagent may be kept for years unimpaired in strength if contained in glass bottles provided with well-fitting glass stoppers; access of air causes decompn. The most sensitive prepn. of the reagent for localizing K in living cells is made by dissolving 20 g. pure Co nitrite and 35 g. NaNO_2 in 75 cc. dil. AcOH (10 cc. glacial AcOH + 75 cc. H_2O). This soln. even reacts with a 0.001 *N* KCl soln. The microscopical prepn., treated with the reagent, is mounted in a mixt. of $(\text{NH}_4)_2\text{S}$ and glycerol on a glass slide.

R. BRUTNER

Action of chloroform on syphilitic serum. GALESCU AND CONSTANTINESCU. *Gaz. hebdomadaire des sciences médicales de Bordeaux* Nov. 5, 1922; *Répert. pharm.* 34, 353(1922).—To test for syphilis where the equipment necessary for the Wassermann test is not at hand add 1 cc. of CHCl_3 to 1 cc. of the serum in a test-tube and shake gently. The reaction is positive when a yellow, compact ring forms at the surface of contact of the 2 liquids and the lower CHCl_3 layer has an emulsified appearance. It is negative when there is no ring formation and when the CHCl_3 layer remains limpid. The reaction is physico-chem. in nature, and depends on the fact that the colloidal complex responsible for the Wassermann reaction is insol. in CHCl_3 . A. G. DuMEZ

A colorimeter for bicolorimetric work. VICTOR C. MYERS. *J. Biol. Chem.* 54, 675-82(1922).—Description of a wedge colorimeter, with magnifying lens and attached lamp house. Three wedges are provided. In ordinary colorimetric estns. only 1 is needed. In bicolorimetric work, as in p_{H} detns. in liquids that are clear and colorless before the addition of the indicator, 2 wedges are used. With similar detns. in colored or turbid solns., the third wedge is employed.

I. GREENWALD

A micromethod for the estimation of acetone and β -hydroxybutyric acid in blood without making a venous puncture. ALFRED LUBLIN. *Klin. Wochschr.* 1, 1748-9 (1922).—Mix 2 cc. of blood with 0.80 cc. of water, 0.30 cc. of 0.66 *N* H_2SO_4 and 0.30 cc. of 10% Na_2WO_4 in a small centrifugal tube, and centrifuge for 1.5 min. Of the clear supernatant liquid transfer 0.75 cc. (= 0.09 cc. blood) to a 50-cc. micro-Kjeldahl flask and add. 25 cc. of H_2O , 1.0 cc. of 10% HOAc and a trace of talcum. Distil for 10 min., collecting the distillate in a 100-cc. Erlenmeyer flask (A) to which has been previously added 15.0 cc. of H_2O , 5 cc. of 0.02 *N* I and 2 cc. of 25% NaOH. Ten min. boiling suffices to drive over all of the preformed acetone. Replace flask A by a second flask (B) that contains an alk. liquid exactly like that originally contained in (A). To the contents of the distg. flask add, drop by drop, 20 cc. of a soln. contg. 2 g. $\text{K}_2\text{Cr}_2\text{O}_7$, 80 cc. H_2O and 2 cc. of concd. H_2SO_4 without interrupting the distn. Distil for 10

min. The β -hydroxybutyric acid is oxidized to acetoacetic acid, which decomposes into acetone and CO_2 in the 2nd stage of the reaction. Det. the unchanged I in flasks A and B by titration with 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$ after acidifying with 2 cc. of 25% H_2SO_4 with starch as an indicator. To convert cc. of I into mg. of acetone, multiply by the factor 0.0483. To convert cc. of I into β -hydroxybutyric acid, multiply by the factor 0.125.

MILTON HANKE

The laboratory preparation of a purified hematoxylin. A. H. DREW. *Brit. J. Exptl. Pathol.* 3, 307(1922).—Com. hematoxylin is boiled with Zn dust to remove an impurity and reduce it to a leuco compd.

HARRIST F. HOLMES

A note on the determination of urea in blood by the Folin and Wu method. A modified apparatus. GEO. G. BOGGS AND W. S. McELLROY. *J. Lab. Clin. Med.* 8, 254-5(1923).—In the detn. of urea in blood by the Folin and Wu method slight variations in pressure cause acid in the receiver to be drawn back into the receiving tube. The authors have modified the original app. in such a way that a slow current of air may be passed into the delivery tube so that a slight positive pressure is maintained and back suction prevented. The air current enters the delivery tube beyond the bend. It was found that no NH_3 was lost even with a moderately fast current of air. E. R. L.

The relative value of some of the commonly used methods for the detection of occult blood in the stool. H. A. REIMANN. *J. Lab. Clin. Med.* 8, 265-70(1923).—With patients on unrestricted diet all stools are positive to both benzidine and guaiacum. A positive reaction is valueless unless the patient has been on a meat-and-chlorophyll-free diet for 3 days, and has had thorough evacuations for at least 3 days prior to the test. R. found that by the Gregerson technic of the benzidine test one part of blood in 12,000 could be detected, by the guaiac test one in 1200, and by the spectroscopic one in 60. The most convenient method was considered the Gregerson technic checked by 1 to 60 soln. of guaiacum in alc. By the use of both tests some idea of the extent of an intestinal hemorrhage may be obtained. It was found, for example, that a positive guaiacum test could be obtained after the oral administration of 2 cc. of blood, but not after 1 cc.

E. R. LONG

The quantitative estimation of iodine in urine. H. LARUE MARSH. *J. Lab. Clin. Med.* 8, 271-2(1923).—The method is recommended for the detn. of I in the urine following I therapy. It consists of the detn. of the total halogens in the fused sample by the Volhard-Arnold volumetric method, and the detn. of the chlorides in another sample from which the I had been removed by the method of Gooch. The difference between the 2 figures represents the I present in the urine.

E. R. LONG

A simple method for calculating the basal metabolic rate. R. L. HADEN. *J. Lab. Clin. Med.* 8, 272-5(1923).—In making the calcn. the total amt. of O_2 consumed during the period of the test is divided by the number of min. the test is run, to give the O_2 consumption per min. The factor corresponding to the nearest temp. and nearest barometer reading is found in a table of factors given. This factor represents the following: $(TC \times BC \times 60 \times 4.825)/1000$, where TC is the correction for temp. and BC the correction for barometric pressure. The product of this factor by the O_2 consumed per min. in cc. represents the total heat production. This has only to be divided by the surface area as detd. from the DuBois chart and compared with the normal for that age and sex.

E. R. LONG

Some sources of error in the determination of chlorides in blood and similar material. ISIDOR GREENWALD AND JOSEPH GROSS. *J. Biol. Chem.* 54, 589-94(1922).—The most accurate figures for the amt. of chloride in blood are obtained when the amt. of chloride is calcd. from the detn. of the excess Ag in the filtrate from the Folin-Wu H_2WO_4 pptn. The method described by Whitehorn (*C. A.* 15, 1323) in which this filtrate is used seems to be the most desirable for routine detns. The values thus

obtained agree very well with those obtained by digestion of the whole blood with HNO_3 and AgNO_3 . High values are obtained in the picric acid methods owing to the formation of a purine-Ag picrate. Other precipitants, such as HNO_3 , *m*-phosphoric acid and $\text{CCl}_3\text{CO}_2\text{H}$, give low results which may be assumed to be due to the presence of some org. Cl compd. in the blood which is pptd. by the reagent. H_2WO_4 apparently decomposes this org. Cl compd. giving Cl ion. When CuSO_4 and NaOH and $\text{Ca}(\text{OH})_2$ are used there is a slight amt. of basic Cu chloride formed which makes the results somewhat low.

A. P. LOTHROP

The use of iodine in the determination of glucose, fructose, sucrose and maltose. F. A. CAJORI. *J. Biol. Chem.* 54, 617-27 (1922).—Methods are described for the detn. of glucose in the presence of fructose and sucrose by the oxidation of glucose to gluconic acid with excess of I in the presence of 1-1.5% Na_2CO_3 ; for the detn. of glucose and fructose in the presence of sucrose by oxidation of the 2 sugars by $\text{Cu}(\text{OH})_2$; and for the detn. of the sucrose present by the reduction of either I or $\text{Cu}(\text{OH})_2$ after hydrolysis with 1% HCl at 60° for 2 hrs. The methods are accurate for the detn. of the individual sugars to within 3%. Expts. were also conducted which indicate that maltose can also be detd. by the increase in glucose content of the soln. after digestion with yeast maltase as it is not changed during the acid hydrolysis of sucrose at 60° . A. P. L.

Chart for the conversion of colorimetric readings into hydrogen ion concentration. J. F. McCLENDON. *J. Biol. Chem.* 54, 647-53 (1922).—The degree of dissociation of the indicator in the unknown is detd. by comparing the color produced with that of the indicator in alk. distd. H_2O in which the salt of the indicator is largely, and under certain conditions, 100% dissociated according to Ostwald's hypothesis. A chart has been constructed by means of which it is possible directly to interpret this in terms of the H-ion concn. of the soln. It is, thus, unnecessary to have available buffer mixts. of known H-ion concn. The original must be consulted for details. A. P. LOTHROP

A simple method for the detection of bile acids in serum and in urine. A. I. IGNATOWSKY. *Wiener klin. Wochschr.* 35, 958-9 (1922).—The lowering of surface tension of fluids by bile acids is the principle utilized in this method and the app. employed is Czapek's capillary manometer. By means of a curve given in the text a quant. estn. is possible. The method is greatly weakened by the large number of substances (drugs) which may respond to the test.

W. A. PERLZWEIG

The comparative effects on tissues of isotonic saline and distilled water when used as solvents for mercuric chloride and formal in histological fixation. H. M. CARLETON. *Quart. J. Microsc. Sci.* 66, 501-8 (1922).—Six % solns. of HgCl_2 in either normal saline or distd. H_2O are equally effective for use in histological technic. Tissues are fixed better in normal saline solns. of HCHO (5%) than in distd. H_2O solns. C. H. R.

Effect of the dilution fluid upon red cell counts. B. BEHRENS. *Arch. ges. Physiol.* (Pflüger's) 195, 266-87 (1922).—Erythrocyte counts of various animals made with a variety of dilg. fluids indicate that Hayem's soln. is as satisfactory as any. G. H. S.

Spectroscopy of hemoglobin in the living animal. R. H. KAHN. *Arch. ges. Physiol.* (Pflüger's) 195, 361-5 (1922).—The eye of a curarized albino rabbit is treated with cocaine and illuminated. The light passing through is examd. spectroscopically and changes in the hemoglobin are observed. It is possible to follow the complete transformation of oxyhemoglobin into methemoglobin within the animal body. C. H. S.

Use of the ninhydrin reaction with microscopical preparations for the recognition of lower protein compounds. I. Liver. II. Blood. W. BERG. *Arch. ges. Physiol.* (Pflüger's) 195, 543-54 (1922).—The presence of protein decompn. products in histological sections can be demonstrated by the ninhydrin reaction. C. H. S.

Salting out of polysaccharides and the course of the acid hydrolysis of starch. HANS PERGER. *Arch. ges. Physiol.* (Pflüger's) 195, 92-112 (1922).—Starch and its

decompu. products can be salted out with MgSO_4 or $(\text{NH}_4)_2\text{SO}_4$. The Mg salt is about twice as effective as the other. When a starch paste is being hydrolyzed by 1% HCl the reaction proceeds so rapidly that within $1/2$ hr. no substances precipitable by MgSO_4 remain, as only starch and the more complex split products are thrown down. In the acid hydrolysis of starch the latter is split asymmetrically into compds. of varying mol. size, not first into 2 mols. of equal size and then each of these into 2 more of the same nature, etc. The rate of the hydrolysis increases as the mol. wt. of the materials becomes smaller.

G. H. S.

A new method of staining blood cells and blood parasites. H. EPSTEIN. *Centr. Bakt. Parasitenk.*, I Abt. **88**, 164-8(1922).—The new method depends on the polychromic properties of toluidine-blue. The stain is prepd. as follows: 1 g. of Li citrate is dissolved in 100 cc. distd. H_2O . In this soln. is dissolved 1 g. toluidine-blue. A colloidal ppt. is formed. The soln. is filtered through a moist filter paper and is used as the stain. Blood smears are fixed in MeOH and stained 10-30 mins. After washing in H_2O they are counterstained in a satd. aq. soln. of picric acid for 1-3 sec. They are then washed several secs. in water and dried.

JULIAN H. LEWIS

ABDERHALDEN, EMIL: *Handbuch der biologischen Arbeitsmethoden—Chemische Methoden—Nachweis, Isolierung, Abbau- und Aufbaustudien auf dem Gebiete der Gerbstoffe.* K. FREUDENBERG. *Isolierung, Nachweis und Abbaustudien auf dem Gebiete der Gerbstoffe.* E. SIEBURG, 439-584 pp. M 78. *Spezielle analytische und synthetische Methoden—Phosphatide, Fette, Sterine.* M 108. *Spezielle analytische und synthetische Methoden—Eiweissabbauprodukte und verwandte Verbindungen. Allgemeine Technik und Isolierung der Monoaminosäuren.* M 102. *Methoden zum Nachweis und zur Erkennung ungesättigter Verbindungen.* H. BAUER. M 15. Reviewed in *Z. physik. Chem.* **101**, 329(1922). *Darstellung von Blutfarbstoffen.* F. N. SCHULZ. *Die Eisenhaltige Komponente des Blutfarbstoffes. Ihr Nachweis und ihre Derivatestudie auf dem Gebiete der Porphyrine—Die Abbau des Hämatins und der Porphyrine und die Synthesen der Spaltungsprodukte—Synthesen mehrkerniger Pyrrolderivate und die Konstitution des Hämins-Gallenfarbstoffe und Abbauprodukte des Bilirubins.* W. KÖSTER. 350 pp. M 43.20. Reviewed in *Gazz. chim. ital.* **52**, 166(1922). *Kautschuk und Flechtenstoffe.* E. FORNROBERT, C. HARRING, V. GRAPE AND W. BRIEGER. 438 pp. M 120. Reviewed in *J. Soc. Chem. Ind.* **41**, 109R(1922). *Prüfung der georäuchlisten Lösungen und Reagentien auf Reinheit.* PAUL HIRSCH. *Das Arbeiten mit optischaktiven Kohlenstoffverbindungen.* Egon EICHWALD. *Methoden zu Untersuchungen auf der Gebiet der Tautomerie und Desmotropie.* JULIUS SCHMIDT. M 30. Reviewed in *Z. physik. Chem.* **101**, 329(1922). Berlin and Vienna: Urban & Schwarzenberg.

C—BACTERIOLOGY

A. K. BALLS

Investigations on thallium action. A. BUSCHKE AND F. JACOBSON. *Deut. med. Wochschr.* **48**, 859-60(1922).—Metallic Tl is put on a plate culture of various bacteria. No growth occurs within a circumference of 7-14 mm. Where the inhibiting action ceases a zone of particularly strong growth is seen. With fungi this action is not observed. The action on bacteria occurs in spite of the fact that a soln. of the salts is not of great bactericidal power. For instance a Tl_2CO_3 soln. 1:1000 is necessary to inhibit the growth of *B. coli*. Cf. *C. A.* **17**, 589.

S. AMBERG

Isopropyl alcohol as disinfectant of hands. G. BERNHARDT. *Deut. med. Wochschr.* **48**, 68-9(1922).—Expts. comparing isopropyl and Et alcs. with regard to their power

of disinfecting hands show isopropyl alc. can replace EtOH. It acts in somewhat smaller concn.

S. AMBERG

Propyl alcohol as disinfectant. J. CHRISTIANSEN. *Deut. med. Wochschr.* **48**, 358(1922).—C. has used *n*-propyl alc. as disinfectant for hands and for skin affections for 4 years. Disinfection by alc. is dependent on surface tension and hydrate formation.

S. AMBERG

Indole and phenol formation by bacteria. M. NEISSER. *Münch. med. Wochschr.* **68**, 1384-5(1921).—All bacteria can form indoleacetic acid from tryptophan, but all cannot form indole. Those forming indole cannot do so from indolacetic acid. All bacteria which form indole and phenol from tyrosine happen to be Gram-negative.

S. AMBERG

The d'Herelle phenomenon. R. OTTO AND H. MUNTER. *Deut. med. Wochschr.* **47**, 1579-89(1921).—The bacteriolytic (bacteriophagic) agent can be obtained from cultures alone without infection of animals and without culturing with filtrates from feces.

S. AMBERG

Sensitization experiments on bacteria. A. SCHNABEL. *Deut. med. Wochschr.* **48**, 654-5(1922); cf. *C. A.* **17**, 121.—The tests are made with methylene blue, which is changed to its leuco base by the action of living bacteria. Bacteria are grown on media to which various amts. of substances injurious to the bacteria have been added. The next day the amt. of this substance necessary to inhibit the action of the bacteria on methylene blue is detd., and compared with control cultures. Frequently bacteria grown on media contg. the substance to be tested show a hypersensitiveness; this is sp. to a certain extent. Those grown at higher concns. show a specific decrease of resistance. At a certain concn. of the substance the bacteria may be "fast." For instance, a pneumococcus may become aspecifically hypersensitive when grown at a concn. of optochin 1:200,000, become fast at 1:500,000 and specifically hypersensitive (*i. e.*, to optochin) at 1:5,000,000. Another pneumococcus culture may present different figures.

S. AMBERG

The nature of d'Herelle's bacteriophage. R. OTTO AND F. WINKLER. *Deut. med. Wochschr.* **48**, 382-4(1922); cf. *C. A.* **17**, 298.—The bacteriolytic agent can be obtained more readily by using Berkefeld filtration in place of the centrifuge. Antisera were obtained with lysin (bacteriophage) of Flexner dysentery and other bacilli. The antisera were tested against different antigens by means of the complement fixation method. The antigens were lysin, bacillary emulsions, and exts. from living and dead bacteria. The antilytic serum possesses some antibodies in common with the anti-bacterial sera, but in addn. a sp. antibody which reacts much more with the lysin. Nothing in these expts. contradicts the assumption that the active agent of the d'Herelle phenomenon consists of minute bacterium protein particles, which are formed on decompn. of the living bacteria.

S. AMBERG

Hydrogen-ion concentration and pathogenic power of streptococci. C. F. VAN OYEN. *Tijdschr. vergel. Geneeskunde* **8**, 148-77(1922).—Streptococci are isolated in 2 cases of mastitis of cows from the secretion of the diseased udder. The final p_H in 1% lactose broth and in 1% glucose broth, after inoculations with these 2 strains, is 4.5 or 4.48; both strains produce a "mastitis catarrhalis" after injection into the teat of a cow. The observation of Avery and Cullen that the mastitis-streptococci produce a $p_H = 4.5$ is, therefore, confirmed by these expts.

R. BEUTNER

Comparative studies of the resistance of tubercle and related bacilli to chemical decolorization. H. SCHLOSSBERGER. *Beir. Klin. Tuberkulose* **50**, 144-61(1922).—There is a certain relationship between guinea pig pathogenicity and acid fastness. This was clearly seen in expts. in which pathogenic passage strains were compared with the original cultures. The difference was most marked with original strains which

were of saprophytic nature and only produced local infiltration nodules in large doses. There was a definite relation between the grade of acid and Na_2SO_3 resistance on the one hand and the time of residence of the strain in the warm-blooded organism. Saprophytic strains of acid-fast cultures were not poorer in extractable fat or wax than genuine tubercle bacilli. Therefore, the waxy capsule of the tubercle bacilli does not account for its acid fastness. It is believed that the fat in the internal protoplasm which is difficultly extractable is responsible for the characteristic staining property, and the increased ability to retain the dye as a result of animal passage is due to a dispersion or surface tension increase of the colloidal parts of the cytoplasm. These changes are to be viewed as adaptation phenomenon arising from external influences. H. J. C.

The action of amines on fermentation. J. ORIENT. *Biochem. Z.* 132, 352-61 (1922).—One % solns. of amines were added in various amts. from 1 to 4 cc. to mixts. of 2 cc. glucose soln. and 3 cc. yeast suspension (20%) in nutrient soln. All mixts. were brought to the same diln. by the addn. of nutrient soln. The effects of the amines were detd. by the CO_2 production after 2, 4 and 24 hrs. Of the Me derivs. of the monoamines, methylamine retarded fermentation in dil. soln. and accelerated in concd. The inhibition in dil. soln. was greater than with the other methylamines. Both di- and tri-methylamine stimulated fermentation in concd. soln. as well as in dil. soln. All 3 amines when present in 4.8% concn., as regards dry yeast, retarded alc. fermentation; it was increasingly retarded with increasing Me groups. Choline and its deriv., muscarine, acted as did the monomethylamines, first activating, then retarding and finally activating again in 8% soln. Betaine is harmful in dil. solns. All 3 amines when present as 4.8% of the dry yeast were toxic, and the more so the greater the difference from choline by oxidation. Pentamethyldiamine caused similar reactions. Guanidine simulated choline in its effect. Creatine in weak concn. was strongly inhibitory. Delfuin, curare, aldehyde ammonia and resorcinol were also studied. In general it was found that when the compds. were present at a 4.8% concn. of the dry yeast inhibition was produced and that the intensity of the fermentation decreased with increasing methyl groups and oxidized radicals. F. S. HAMMETT

Biochemical studies of the tubercle bacillus. K. G. DERNBY AND C. NÄSLUND. *Biochem. Z.* 132, 393-411 (1922).—Detns. were made of the growth and proteolytic process of tubercle bacilli under various exptl. conditions. Both human and bovine strains were used. The organisms grow in nutrient media at p_{H} from 4.5 and 8. The optimum p_{H} was between 6 and 6.5 and hence this should be taken as the initial reaction for nutrient media. During growth the H-ion concn. decreases and the curve of titratable acidity runs almost parallel with the p_{H} curve. In old cultures of human organisms contg. glycerol the p_{H} falls again. This does not happen in similar cultures of bovine organisms. The bacilli show very weak proteolytic activity, and only in old cultures is an increase in amino-acid N notable. The filtrate from cultures has no action on peptone or gelatin. Macerated and autolyzed bacilli do not liquify gelatin except when on the acid side of neutrality. This slight action may be due to a pepsin like endoenzyme. Autolyzed bacilli produce a weak splitting of Witte peptone, the optimum point lying close to neutrality. Therefore, endotryptase is present in the organisms. The resistance of tuberculin towards H- and OH-ions was tested in the zone between p_{H} 2.5 and 10.5 by incubation at 37° for 1 week. The tuberculin is not affected save to a minor degree in the most alk. media. The substance is there quite resistant and hence differs from other similar toxins such as the diphtheria or tetanus toxin. F. S. HAMMETT

Adaptation of diphtheria bacilli to hydrogen- and hydroxyl-ions. K. G. DERNBY AND S. SJÖE. *Biochem. Z.* 132, 412-9 (1922).—Diphtheria bacilli can develop in a p_{H} zone from 5.8 to 8.2 at 37° . The optimum falls between 7.2 and 7.6. If the organ-

isms are previously treated with solns. of more acid or more alk. reaction they can be easily adapted to the changed environment. When they are habituated to an increased H-ion concn. the p_H limits as well as the optimum range are moved towards the acid side. The constancy of the growth curve is therefore only relative. It is therefore necessary to keep stock cultures at a reaction not far from the reaction of the stock bouillon. Mixed cultures were used in these expts.

F. S. HAMMETT

The influence of nutritive conditions of the liquefaction of gelatin and indole formation by bacteria. O. ARNBECK. *Biochem. Z.* 132, 457-79(1922).—Of a group of easily assimilable foodstuffs, N-free glucose tends to hinder the liquefaction of gelatin as well as indole formation by a number of bacterial strains. Inhibition of gelatin liquefaction by *Bact. vulgare* (X19) is caused by 0.1% glucose and of indole formation by *B. coli* by 0.08%. Gelatin liquefaction is affected more easily than is indole formation since 0.1% glycerol stops the former but not the latter. The production of liquefying enzymes is favored by the presence of free NH_3 . The fixed alkalis and compds. which liberate alkali (salts of org. acids) act similarly, since they set free NH_3 . Corresponding facilitation of indole formation is not detectable. The free acids formed in sugar fermentation only injure the gelatin liquefaction and indole formation. Other end-products of metabolism play no role. The ability to split gelatin can be lost for some time through the influence of the acids formed from the sugar fermentation. Motility and colonizing are lost in the presence of sugar but only for the duration of its action.

F. S. HAMMETT

The problem of the "economic coefficient" in *Aspergillus niger*. V. BUTKEVICH AND FR. V. G. ORLOV. *Biochem. Z.* 132, 556-65(1922).— $ZnSO_4$ in cultures of *A. niger* produces a marked acceleration of mycelial development and an increase in the "economic coeff." The presence of $ZnSO_4$ in such cultures induces a decrease in acidity and oxalic acid content even to the point where the latter is completely lacking. The optimal temps. for mycelial development and the "economic coeff." are not identical. The latter is lower than the former. The stimulating effect of Co and Hg salts differs somewhat from that of $ZnSO_4$. A wide variability in $ZnSO_4$ concn. (from 0.0025 to 0.005% and from 0.025 to 0.10%) does not cause marked differences in the degree of stimulation.

F. S. HAMMETT

Further contribution on the equivalent formation of acetaldehyde and glycerol in the second type of fermentation. C. NEUBERG, J. HIRSCH AND E. REINFURTH. *Biochem. Z.* 132, 589-96(1922).—Exptl. confirmation is given that the gravimetric detn. of aldehyde coincides completely with the titrimetric results, and that both methods demonstrate the equiv. formation of AcH and glycerol in the 2nd type of fermentation.

F. S. HAMMETT

The growth of rickettsia, the organism responsible for spotted fever, on a solid nutrient medium. M. H. KUCZYNSKI. *Klin. Wochschr.* 1, 1412-13(1922).—The medium used consisted of 1 part of blood serum and 2 parts of nutrient base to which sufficient agar has been added to permit slanting. Sterilization was effected at 56°. The serum of the guinea pig, rabbit, sheep, horse, or pig, can be used. The nutrient base consisted of a 3% nutrient agar having the following compn.: peptone 5.99, amino acids 11.73, inorg. salts 8.42, and glucose 1%. The final p_H of the medium was 7.3. The organisms grow poorly on this medium immediately after they are isolated from the infected animal. They grow very well, however, after a no. of transfers. The isolated organism, when injected into a guinea pig, gives rise to the typical spotted fever syndrome. From the pig the bacterium can then be transferred to the nutrient agar, where it grows as before. The organism loses in virulence after a no. of such cycles.

MILTON HANKE

The nature of the phenomena of d'Herelle. CARL PRAUSNITZ. *Klin. Wochschr.*

1, 1639-42(1922).—The bacteriophage of the dysentery bacillus consists of colloidal particles whose size is similar to that of collargol, namely $20\ \mu\mu$. Pepsin, trypsin, and invertase are composed of much smaller particles. CHCl_3 , C_2HCl_3 , C_2HCl_4 , C_2Cl_6 and toluene do not destroy the action of the bacteriophage. NaF and KCN reduce the action slowly. Tetralin, although it has no deleterious effect upon the enzymic activity of pepsin, trypsin, and invertase, destroys the action of the bacteriophage completely. An antibacteriophagic serum, obtained from rabbits that have been immunized with the bacteriophage, can be deprived of its bacterial antibody but not of its antibacteriophagic properties, by treatment with an emulsion of dysentery bacilli. It is possible to cultivate a completely serum-fast strain of bacteriophage by repeated inoculation from a partially neutralized bacteriophageantibacteriophagic mixt. The bacteriophage is an ultraviolet virus.

MILTON HANKE

Mechanism of the reversal in reaction of a medium which takes place during growth of *B. diphtheriae*. C. G. L. WOLF. *Biochem. J.* **16**, 541-7(1922).—In a bouillon peptone medium of $p_H = 7.8$, during the earlier period of growth the reaction becomes more acid, often exceeding the neutral point of $p_H = 7.0$. A sudden change in reaction occurs when this acid point is reached and the medium becomes alkaline. The alkalinity may reach the high value of $p_H = 8.6$ or even 8.8. It is during the period of alkalinity that the toxin is formed. The reversal of reaction in carbohydrate-free media caused by the growth of *B. diphtheriae* is due, in its acid phase, in part to the production of volatile acids. When the medium becomes alk., it is because the acids are converted into carbonates. Org. acids such as malic and succinic may be utilized to produce carbonates. Formic acid does not seem to be an intermediary product.

BENJAMIN HARROW

The isolation and preservation of tubercle bacilli by means of glycerol. C. C. TWORR. *Lancet* **1922**, II, 1221.—Glycerol is used to destroy contaminating bacteria in the isolation of the tubercle bacillus from sputum and tissue.

E. R. LONG

Uses of hydrocyanic acid in disinfection. WOLF. *Öffentl. Gesundheitspflege* **7**, 126-31(1922); cf. C. A. **16**, 2379.—The uses of HCN in disinfection procedures, together with the sp. activities of certain derivs. of, or combinations with HCN, are discussed. The facts disclosed are largely taken from the literature.

G. H. S.

The effect of various culture media upon acid production by *B. lactis aerogenes*. E. WOLFF. *Z. Kinderheilk.* **31**, 226-35(1922).—In culture media of varying sucrose concn. (from 1 to 20%) and const. peptone content the acid production of *B. lactis aerogenes* remained practically const. With a const. sugar content and variable amts. of peptone the acidity was proportional to the amt. of peptone. In a whole milk medium with 12-17% sugar the acid formation decreased as the concn. of sugar increased.

G. H. S.

Intestinal bacteria. V. Nutritional physiology of *B. bifidus*. A. ADAM. *Z. Kinderheilk.* **31**, 331-66(1922); cf. C. A. **16**, 948.—The peculiarities of the bacterial cells are referable to their metabolism, since to develop normally *B. bifidus* requires definite fat, protein, and carbohydrate components of milk. While the use of carbohydrates is not restricted closely, the chem. structure of the sugar is important; monosaccharides favor growth, but to a less degree than disaccharides. Lactose, maltose, and sucrose are most readily utilized. Of the proteins, casein is most satisfactory. Of the fats, Na oleate and butyrate are best. Lactic acid salts, neutral fats, and peptone and tyrosine stimulate growth. Multiplication is inhibited or growth is rendered abnormal by such substances as starch, dextrin, hexosediphosphoric acid, pyruvic acid, acetates and acetaldehyde, glycerol, oleic and butyric acids, albumin, aliphatic amino acids (glycine, alanine, leucine), asparagine, and Ca soaps.

G. H. S.

Reverse selective bacteriostatic action of acid fuchsin. J. W. CHURCHMAN. *J.*

Exptl. Med. 37, 1-10(1923).—Acid fuchsin possesses a bactericidal power, selective as between Gram-negative and Gram-positive spore-bearing aerobic organisms. The selective feature is the reverse of that of gentian violet. This reverse selective activity is also possessed by simpler sulfonated substances and would appear to be dependent in some way on the presence of SO_3 radicals. Selective penetration, if at all concerned in the behavior of gentian violet and fuchsin towards bacteria, must play a minor role. In the case of gentian violet the power to kill organisms and the power to prevent their growth run, so far as the selective feature is concerned, parallel. In the case of acid fuchsin, the bacteriostatic and bactericidal selective features do not run parallel. *Bacillus pyocyaneus*, an organism resistant to gentian violet, is quite susceptible to acid fuchsin. This organism is the cause of annoying and persistent infections in wounds. The observations on the effect of sulfonated substances may give a lead as to the control of these infections.

C. J. WEST

D--BOTANY

R. M. DUGGAR

The application of colloid chemical methods to plant pathology. F. BOAS AND F. MERKENSCHLAGER. *Centr. Bakt. Parasitenk. Abt. II* 55, 508-15(1922).—The proteins of the plasma expressed from 10 to 12 day sprouts of *Lupinus luteus* were pptd. by KCl and MgCl_2 . The action of these salts depended on the cation. CaCl_2 had little or no action. Carbohydrates acted protectively toward the action of KCl and MgCl_2 . These salts also act harmfully *in vivo* in that the structure and, thereby, the functions of the plants, are altered. One result is the difficulty in the mobilization of Fe.

JULIAN H. LEWIS

Studies on the mechanism of the physiological effects of certain mineral salts in altering the ratio of top growth to root growth in seed plants. T. W. TURNER. *Am. J. Botany* 9, 415-45(1922).—In working with nutrient solns., barley and corn show significant increases in ratio of tops to roots as NO_3 concn. of the soln. increased. The effect of NO_3 was independent of the total concn. of the soln. and H-ion concn. Flax did not give a similar increase of top to roots with increase of NO_3 . The increased ratio of tops to roots which results from increasing the amt. of NO_3 in soln. may be explained on the basis of increased use of carbohydrates in the tops because the greater N supply produced greater growth. This results in a decrease in the supply of carbohydrates for the roots, which may bring about an absolute or relative reduction of root growth.

J. J. SKINNER

Comparative action of sylvinit and of its components upon the early growth of plants. PIERRE LESAGE. *Compt. rend.* 175, 992-5(1922).—*Lepidium sativum* was grown in Knop solns. except that in *a* was 0.01 N NaCl, in *b* 0.01 N KCl and in *c* a 71/100 g. of sylvinit. Comparing the growths of 10 plants in each culture with those of 10 in distl. water, *d*, the combined lengths of root and hypocotyl were 71, 70, 99 and 63 mm. for cultures *a*, *b*, *c* and *d*, resp. The most favorable concn. of sylvinit for growth was between 0.01 and 0.04. Cultures in 0.01 sylvinit were compared with those in a mixt. of NaCl + KCl in the proportions in which they exist in sylvinit and the growth was found to be 62 to 54 in favor of sylvinit. If to the mixt. of NaCl + KCl, MgCl_2 and CaSO_4 were added in the proportions in which they exist in sylvinit, the growth was 66 to about 57 in favor of the sylvinit. It is apparent that a mixt. of the 4 salts does not contain all of the active plant food elements which exist in sylvinit.

L. W. RIGGS

Influence of selenium and of radium on the germination of seeds. J. STOKLASA. *Compt. rend.* 174, 1075-7(1922).—The expts. were made at a temp. of 23-25° in the

light. Na_2SeO_3 in concns. of 10^{-6} P. M. [P. M. means per gram mol.], or stronger, was toxic toward the germination of buckwheat, oats, vetch, rye, and wheat. Na_2SeO_4 in concns. of 10^{-6} P. M. was favorable to the germination of these seeds and did not show a toxic action until a concn. of $7 \cdot 10^{-5}$ was reached. Seeds supposed to be dry were treated with Ra emanations equiv. to 30 *Mache Units* for 12 hrs., and their germinative qualities compared with suitable controls for a period of 72 hrs. The control seeds showed a germination of 95 to 99% in 144 hrs. Without the emanation the germination ranged from 35 to 69% in 72 hrs.; with the emanation, from 70–99% in 72 hrs. Seeds treated with Na_2SeO_3 in various concns. and subjected to Ra emanations showed from 2 to 3 times as much germination in 110 hrs. as those lacking merely the Ra emanation treatment. Replacing Na_2SeO_3 by Na_2SeO_4 , 10^{-3} P. M. the increase in germination of those receiving also Ra emanation treatment was 1.4–2 times as much in 110 hrs. The smaller relative increase in the latter case was because of the lesser toxic action of Na_2SeO_4 .

L. W. RIGGS

Chemistry of after-ripening, germination, and seedling development of juniper seeds. D. A. PACK. *Bolan. Gaz.* **72**, 139–50(1921).—The microchem. and phys. changes accompanying after-ripening, germination and seedling development of juniper seeds have already been studied (cf. *C. A.* **15**, 3866). Further results are reported in continuation of this work. The material for analysis was prepd. by slightly modifying the method of Lowenstein (cf. *C. A.* **3**, 1971) and Miller (cf. *Ann. Botany* **24**, 693(1910)), and the analytical method of Koch (cf. *C. A.* **4**, 1756). The digestion of storage fats and proteins was accompanied by the synthesis of many formative and metabolic compds., and the rate of formation of these proved the power of enzyme action at 5° . The low temp., by retarding respiration, reduced the combustion to a min., favored the accumulation of cell-building and cell-active compds. and enzymes, and this led to after-ripening. The lipoids decreased 9.7% during after-ripening and 32% during seedling development. The neutral fats sustained this loss. Phosphatides more than doubled during after-ripening. Glycerol and fatty acids were supplied by hydrolysis of fats, and H_3PO_4 and N complexes from inorg. P and protein hydrolysis, resp. A slight decrease in phosphatides occurred in seedling development, perhaps on account of the H_3PO_4 required for nucleic acid. The acid value of the Et_2O ext. and sapon. no. increased and the I no. decreased in after-ripening and seedling development. During the latter, carbohydrate accumulation from unsatd. fatty acids was 20%. The sapon. no. was a min. for seedlings, owing to long chain fatty acids. Dry seed and after-ripened lipoids increased 9.9% and 11.0% in wt., resp., when artificially oxidized. The reducing power of the lipoids increased during after-ripening, and the seedling lipoids increased 3.1% in wt. under similar conditions. Extractives increased during after-ripening and seedling development, owing to increase in amino-acid N, amides, peptides, nucleic acid derivs., alcs., sugars, etc. Ammoniacal N was const. during after-ripening, but decreased during seedling development. This decrease corresponds to the N for forming chlorophyll. Amino N increased 7-fold during after-ripening and 3-fold during seedling development. The ratio amino N/total N was $1/4$ for dry seeds, $1/2$ for after-ripened seeds, and $1/2$ for seedlings. Sugar formation was very slight during after-ripening, but noticeable during germination and seedling development. The reducing sugars (after hydrolysis) increased 0.5% in the after-ripened seeds, with only a few 100ths % of direct reducing sugars. Nearly all reducing sugar in dry and after-ripened seeds was combined with tannins. Dry seeds gave no pentose reaction, but after-ripened seeds and seedlings showed a marked reaction. During seedling development the % sugars increased greatly. Considerable material was unaccounted for, possibly owing to org. acids. The extractives of dry seeds were distinctly acid, those of after-ripened seeds and seedlings very acid. During after-ripening the proteins de-

creased 6% and starch increased 0.2%. Since N was const., chlorophyll N must be derived from other N compds. present. C. C. DAVIS

The influence of immersion in certain electrolytes upon cells of *Saxifraga umbrosa*.

MAUD WILLIAMS. *Ann. Botany* 36, 563-76(1922).—A continuation of earlier work (cf. C. A. 13, 1484). Detns. were made of the times of immersion necessary to produce permeability of cells of *Saxifraga umbrosa* to 0.1% $K_2Cr_2O_7$, different concns. of KI, KNO_3 , KCl, NaI, $NaNO_3$, and NaCl being used. Measurements were made using the "meter bridge" method, a commutator and a galvanometer. The readings were made at intervals extending over a period of 42 days. The permeability changes were not reversible and indicate that damage to the cells resulted. The importance of making the expts. at a definite temp. is shown. The equation, $\log T + k (\log C + 1) = K$, where T = time of immersion required to produce the change and C = concn. in gram-mols. per l., has been shown to hold in the cases examd. for periods up to 4 hrs. for immersions at 25°. This equation as obtained under the conditions noted above agrees in form with that obtained by others for the disinfection of bacteria and for poisoning of *Chlamydomonas* by other chemicals. The const. K and the coeff. k depend upon the salt used and equimol. solns. do not produce equal effects. Evidence is presented favoring the view that the action of the strong solns. employed is connected with the adsorption of ions and the consequent pptn. of colloidal matter. F. C. COOK

Proof of the power of the wheat plant to fix atmospheric nitrogen. C. B. LIPMAN AND J. K. TAYLOR. *Science* 56, 605-6(1922).—"In a series of wheat cultures in solns., we have recently proved conclusively that wheat plants, even in only 6 weeks of growth, can fix large quantities of N from the air. They possess this power whether N is supplied to the roots or not." L. W. RIGGS

Investigations on the nitrogenous metabolism of the higher plants. III. The effect of low-temperature drying on the distribution of nitrogen in the leaves of the runner bean. A. C. CHIBNALL. *Biochem. J.* 16, 599-607(1922); cf. C. A. 16, 3105.—Drying between 30 and 50° causes considerable proteolysis, with increase in the simpler water-sol. nitrogenous products, chiefly NH_3 (in the form of NH_4 salts or as the amide N of asparagine) and monoamino acids. "The predominance given to asparagine as a final product of protein metabolism is based, to a certain extent, on an erroneous conception as to the amt. of it actually present in the living leaf." IV. **Distribution of the nitrogen in the dead leaves of the runner bean.** *Ibid* 608-610.—There is no great withdrawal of N from the leaves to the stems or roots when the plant becomes aged. BENJAMIN HARROW

Physiological studies of effects of formaldehyde on wheat. W. M. ATWOOD. *Botan. Gaz.* 74, 233-63(1922).—1: 320 of CH_2O , used as a fungicide, is at the edge of the danger zone. If, as Hurd believes (C. A. 15, 699), a polymer of CH_2O is deposited on dried treated wheat, and subsequent injury to the grain is incident to the liberation of CH_2O gas from the ppt., with its resultant soln. in the moisture content of the living cells, the process must be a slow, cumulative one; and this is in harmony with the definite, although slow, entry of CH_2O through the seed coat as shown by A. Even at a concn. 1: 320, while germination is often but lightly affected, the diastatic power of wheat is retarded, the catalases are less active, and respiration is definitely reduced. B. H.

Chemistry of the higher fungi. XVI. Fungi lipoids. RUDOLF ROSENTHAL. *Monatsh.* 43, 237-53(1922); cf. C. A. 16, 3109.—The phytosterol isolated from a fleshy fungus (*Amanita muscaria*) is proven to be identical with ergosterol isolated by Tanret from *Claviceps purpurea*. This adds 4 atoms of I and thus contains 2 double bonds. The cerebrin from *Amanita muscaria* forms a powder, m. 135-6.5°. It contains 73.44% C, 12.85 H and 2.52 N, and is resistant to hydrolysis by aq. acids or alkalis. The orcin test is negative (no sugar present). The acetate forms needles, m. 62-3°. Upon sapon.

a cerebrin was obtained which was similar in compn. to the original product, but which melted at 118-21°. Hydrolysis with MeOH-Ba(OH)_2 gave an acid, m. 95°, contg. 74.83% C, 12.99 H and 1.38 N. The Mg salt is insol. in hot alc. The mother liquor of the hydrolysis gave a ppt. with picric acid, indicating a base, but no analysis was obtained. Apparently the same cerebrin was obtained from *Hypholoma fasciculare*.

C. J. WEST

Urease and urea in fungi. A. GORIS AND P. COSTY. *Compt. rend.* 175, 539-41 (1922).—From 0.5 to 1.0 g. of a fungus is placed in a 60 cc. sterile flask with 30 cc. of a 0.1 N soln. of urea in water satd. with toluene. Each flask is plugged with a cotton carrying a strip of moist litmus paper. Control flasks contained urea or fungus alone. These flasks were placed in a thermostat at 37° and were observed from hr. to hr. as certain species which gave a negative reaction at the end of the first hr. yielded a positive result later. The activity of the enzyme is estd. by titration with 0.1 N HCl. The activity varies with the species and with the part of the fungus employed, the hymenium being far more active than the foot or head. Urease exists in nearly all genera of fungi, and so far has been found in about 200 species. *Amanita* and *Lepiota* so far as examd. gave negative results. Urease was absent from *Lycoperdon*, *Pluteus cervinus*, and 5 other species, each of which contained urea. The urea was detd. by extg. 10 g. of finely ground fungus with boiling 90% alc. for 15 to 20 min. on the water bath. The liquid was expressed and evapd. in a vacuum to remove the alc. and after filtering through paper previously moistened with the liquid, the urea was pptd. with xanthidrol. The proportion of urea in 23 species ranged from 0.28 to 9.23 parts in 1000. The urea content varies with the stage of growth. L. W. RIGGS

Urease and urea in fungi. A. GORIS AND P. COSTY. *Compt. rend.* 175, 998-9 (1922).—By the method previously reported (cf. preceding abstr.) the urease was estd. in the foot, cap and hymenium. The figures quoted in the following represent the no. of cc. of 0.1 N HCl necessary to neutralize the $(\text{NH}_4)_2\text{CO}_3$ formed by the decompn. of 0.1 N urea by a given wt. of the fungus tissue. Twelve fungi were tested. The activity of urease in the stalk ranged from 0.2 in *Boletus scaber* to 3.3 in *Boletus edulis*, av. 0.97. In the cap the range was 0.4 in *B. scaber* to 5.5 in *B. edulis*, av. 1.4, and in the hymenium the range was 0.8 in *Hydnum umicium* to 7.5 in *B. edulis*, av. 2.87. In prep. a soln. of urease from the hymenium of *Boletus*, samples from old fungi giving yellow solns. should be sepd. from young fungi which give white solns. The soln. is mixed with CaCO_3 and an equal vol. of glycerol is slowly added with mixing; the mixt. is allowed to stand 48 hrs. in the cold and is then filtered. L. W. RIGGS

Anthocyanic pigments and phlobatannins in plants. Sr. JONESCO. *Compt. rend.* 175, 904-7 (1922).—The object of this study was to learn the relations, if any, between the anthocyanic pigments and those related to tannin. Complete details of the work will be given in a future paper. Red leaves of *Prunus pissarai* were dried and powdered and, after complete extn. of chlorophyll, were exhausted for 2 weeks with Et_2O . The Et_2O ext. contained a colorless substance crystg. in long plates or needles very sol. in water which gives the reactions of the tannins, also a yellow amorphous substance insol. in hot or cold water but very sol. in alc. which does not give the reactions of the tannins. After the extn. of these 2 substances the leaves yielded anthocyanidins and pseudo-bases on extn. with AcOEt and amyl alc. These substances are fine amorphous powders, insol. in water, Et_2O or H_2SO_4 , slightly sol. in HCl, freely sol. in AcOH , AcOEt amyl alc. and the alkalis. Yellow pseudo-bases heated with dil. HCl are transformed into a red pigment, an anthocyanidin. L. W. RIGGS

Influence of the constitution of the nutritive media upon the composition of *Aspergillus niger*. ÉMILE-F. TIERROINE, R. WURMSER AND J. MONTANÉ. *Compt. rend.* 175, 541-4 (1922); cf. C. A. 16, 3931.—The total N in *A. niger* decreases with the de-

velopment of the fungus, but does not vary with the concn. of N in the nutritive medium. Except in young cultures, in which there is an increase in total N with an increase in the carbohydrate constituent (glucose or sucrose) of the nutritive medium, the total N decreases with an increase of carbohydrate in the food, the N of the food being constant at 5 parts $(\text{NH}_4)_2\text{SO}_4$ per 1000. The substitution of urea or NaNO_3 for $(\text{NH}_4)_2\text{SO}_4$ in the nutritive medium resulted in a slight decline in the total N. Peptone and guanidine substituted for $(\text{NH}_4)_2\text{SO}_4$ caused a decline of 18.3 and 45.0%, resp., in the total N of the fungus. With the N constant as above, xylose, arabinose and galactose were severally substituted for glucose. The first 2 caused no change, but galactose caused a reduction of 21% in the total N. The mycelium obtained by a normal culture was washed and placed in the medium of Czapek with glucose (N starvation) or with neither sugar nor N, and maintained at 37° for 5 days. The loss of N was over 50%. These results suggest a resemblance between the physiology of *A. niger* and that of animals. Also in *Bull. soc. chim. biol.* 4, 623-43 (1922).

L. W. RIGGS

Transformation of the chromogen of the yellow flowers of *Medicago falcata* by the action of an oxidase. S. JONESCO. *Compt. rend.* 175, 592-5 (1922).—To prove that oxidases bring about the formation of a pigment from the yellow chromogen of this plant, J. submitted the extd. pigment to the action of the oxidase obtained from *Russula delicata*, and obtained a violet color very similar to that of the natural pigment. Mild oxidizing agents also gave the color, but reducing agents did not. The chromogen gave reactions characteristic of a phenol.

J. J. WILLAMAN

The relation between anthocyanin and oxidase. M. MIRANDE. *Compt. rend.* 175, 595-7 (1922); cf. preceding abstr.—In the lily bulb, oxidases convert a chromogen into anthocyanin. Only those cells which contain oxidase can produce the pigment. Inert gases and vacuum prevent its formation.

J. J. WILLAMAN

Fate of carbohydrates upon the death of leaves of trees. RAOUL COMBES AND MILLE DENTSE KOHLER. *Compt. rend.* 175, 590-2 (1922); cf. C. A. 17, 125.—It has already been shown that a portion of the carbohydrates contained in leaves at the end of growth is consumed by respiration during autumnal yellowing, a portion is extd. by rain or dew, and a portion remains in the leaf when it falls. The object of this study was to det. the portion of carbohydrate that returned to the living tree during the period from the beginning of yellowing to becoming brown. Leaves were collected from *Fagus silvatica* (1) at the beginning of yellowing, Oct. 19, (2) at the brown stage, Oct. 29, (3) at the beginning of yellowing, Oct. 19, but the stems were placed in water and the leaves allowed to remain near the tree until Oct. 29. The first lot of leaves were analyzed immediately after collection. The 2nd and 3rd lots after Oct. 29. Fifty leaves were collected for each lot. The results in mg. of the analyses of lots 1, 2, and 3 were: reducing sugars 196, 96 and 137, resp., nonreducible carbohydrates sol. in alc. 310, 136, and 196, resp., carbohydrates insol. in alc. and readily hydrolyzable 321, 530 and 492. From these figures it is deduced that the carbohydrates before yellowing were represented by $196 + 310 = 506$, that remaining at the time of fall $96 + 136 = 232$, that removed by respiration and leaching $506 - (137 + 196) = 173$, and that returned to the tree during the 10 days $(137 + 196) - 232 = 101$.

L. W. RIGGS

Characteristic proteins in high- and low-protein corn. M. F. SHOWALTER AND R. H. CARR. *J. Am. Chem. Soc.* 44, 2019-23 (1922).—A comparative study of a Champion White Pearl high-N corn (2.95% N), a high-N popcorn (2.43% N) and a Yellow Dent low-N corn (1.29% N) showed that in the high-N corns a considerably larger part of the protein is present as zein and globulins which have been formed at the expense of the amides, albumin and gluten. The embryo makes up about 15% of the total wt. of high-N corn grain while dent corn of the usual compn. has only about 11% of embryo. Zein is the protein which varies most, averaging 50.28% in high- and

31.85% in low-N corn, and 57.24% in high-N popcorn. The total N content seems to det. the amts. of the various proteins. The amino N in the filtrate from the bases is higher in the high- than in the low-N corns. The diamino acids form approx. twice as large a % of the total N in high- as in low-N corns.

C. A. R.

Existence of particular protein bodies in the pollen of divers Asclepiadaceae. L. GUIGNARD. *Compt. rend.* 175, 1015-20(1922).—The evidence presented is mainly histologic, the protein character of the cellular elements in question being shown by its reactions toward Millon's reagent and by other protein tests. In contrast to the starch grains these protein bodies do not disappear during the development of the pollen tube. They are transported to the micropyle of the ovule where it is thought that they are absorbed in harmony with the phenomena which accompany or follow fertilization.

L. W. RIGGS

Presence of aucubin and of melampyrite in several species of Melampyrum. MARIE BRAECKE. *Compt. rend.* 175, 990-2(1922); cf. C. A. 15, 4019; 16, 1451.—Aucubin which was found in *M. arvense* was also extd. from *M. pratense* L., *M. nemorosum* L., and *M. cristatum* L. The amts. were estd. by observing the initial rotatory power of an ext. and the rotations after the action of invertin and emulsin, resp. Melampyrite (dulcite) was found in *M. nemorosum* and *M. cristatum* but not in *M. pratense*.

L. W. RIGGS

Centaurein, a new glucoside derived from the root of Centaurea jacea L. MARC BRIDEL and CAMILLE CHARAUX. *Compt. rend.* 175, 833-5(1922).—The greater portion of the glucoside is contained in the bark and outer portions of the root. Since no enzyme is known that will decompose the glucoside, the latter is extd. from the outer part of the air-dried roots as follows: The material is pulverized and extd. with 4 times its wt. of boiling 90% alc., the alc. is removed and the residue is taken up with boiling water. When the aq. soln. has cooled to 30° it is rapidly extd. twice with ether and the glucoside crystallizes immediately after the sepn. of the aq. soln.; the yield is 2.6% of the dried root bark. Recrystn. is performed by adding the crystals to boiling water, filtering the soln. and cooling the filtrate. Crystn. from alc. gives a product different in water content, m. p., and soly. The name *centaurein* is proposed. It crystallizes in elongated microscopic plates, pale yellow in color and chalky in taste. It contains 9.96% of water which it loses at 50° in a vacuum without apparent alteration. The m. p. is not definite but lies between 168° and 175°. Dissolved in pure anhyd. MeOH it is levorotatory, $\alpha_D = -76.54^\circ$ ($p = 0.1742$, $v = 10$, $l = 2$, $\alpha = -2.666^\circ$). It is almost insol. in water, ether, and CHCl_3 . Sol. in 5% NaOH soln. with golden yellow color, the soln. giving a rotation of -133.68° ($p = 0.2244$, $v = 10$, $l = 1$, $\alpha = -3^\circ$) which corresponds to $\alpha_D = -148.47^\circ$ for the anhyd. product. Centaurein is not a reducing agent. It is slowly hydrolyzed by 5% H_2SO_4 at the temp. of the boiling water bath, but more rapidly on a CaCl_2 bath under a reflux. Upon the hydrolysis of 1.7378 g. of centaurein, there is obtained 0.5854 g. of a reducing sugar, which is entirely glucose, and 1.2300 g. of a cryst. product called *centaureidin*. Emulsin is without action on centaurein. The av. of 2 detns. gives C 53.62, H 5.40, N absent, mol. wt. between 500 and 550.

L. W. RIGGS

Detection and distribution of rhinanthin (pseudoincandin). H. MUELLER. *Pharm. Monatshfte* 3, 149-55(1922).—Of the Scrophulariaceae and Rubiaceae examd. (about 370 species) microchemically, 18% contained this compd.

W. O. E.

Relation between the colloidal state and physiologic functions of protoplasm. RENÉ WURMSER and RAYMOND JACQUOT. *Compt. rend.* 175, 782-4(1922).—Fragments of marine algae were placed for 2 min. in sea water heated from 36 to 45°, then in sea water at normal temp. and were exposed to light. The dissolved O content of the sea water was detd. by the method of Winckler. If the excess of O evolved by the

assimilation of the normal alga over the O used in respiration is represented by 100 the O evolved after heating as above is shown by the following figures:

		36°.	38°.	40°.	42°.	45°.
<i>Ulva lactuca</i>	100	100	62	33	7.2	—1.4
<i>Iridea edulis</i>	100	69.8	25.8	16.4	—26.6	...
<i>Rhodymenia palmata</i> (red)	100	98.9	28.2	4.1	—15.2	...
<i>Codium tomentosum</i>	100	90.9	19	...	—22.3	...
<i>Laminaria saccharina</i>	100	35	—51.4	—57	—50.4	...
<i>Laminaria digitata</i>	100	71.6	—81.2	—81.2
<i>Rhodymenia palmata</i> (green)	100	12.2	—20.3	—16.7	—18.9	...

The respiration of *Ulva lactuca* in the dark at the temps. given in the above table may be represented by the figures 5.0, 3.5, 3.0, 2.6, 1.65, the O being detd. by Osterhout's colorimetric method. These figures are so small compared to those in the above table for *U. lactuca*, that the latter figures represent the variations of photosynthesis. Further heating of the alga from 45 to 65° causes a corresponding drop in the respiration from 1.65 to 0.01. With other algae the decrease in respiration under similar treatment is not so const. as in the case of *U. lactuca*.

L. W. RIGGS

Amylase in plants. I. The formation and behavior of amylase in living plants.

K. SJÖBERG. *Biochem. Z.* 133, 218–93 (1922).—A detailed abstract of this monographic study is not possible. In general the results showed that the activity of the amylase of various plants (the ability to form sugar) follows within wide limits the formula of Euler and Svanberg (*C. A.* 14, 1130). The p_H optimum is between 5.0 and 5.4. During germination and early development of *Phaseolus* a marked formation of amylase occurs in all parts of the plant up to nearly 1000 times as great as the initial value. The highest values were found in the buds and young leaves. The amylase activity of the buds and leaves of a series of trees at different times of year was quant. detd. Here too the activity is greatest in the young leaves. Changes in amylase activity were particularly studied in the conifers or needle-bearing trees. The activity varies in one and the same tree and is too small to be detd. in the young suckers. It undergoes regular changes during the course of the day in the leaves *in situ*. If algae are grown in media which contain starch, Ca lactate and Ca tartrate the amt. of amylase increases. When sucrose, lactose, maltose, glucose or galactose are present the amylase is decreased. A pure inorg. medium exerts no effect on the amylase activity. *Phaseolus* plants grown in culture media show but little change in their amylase content. Apparently there is no clear relation between amylase activity and the amt. of starch or sugar. II. The sensitivity to temperature of the amylase of *Phaseolus vulgaris*. *Ibid* 294–330.—S. found that the optimum reactivity of *Phaseolus* amylase in phosphate-buffered mixts. at 40° is at a p_H of 5.0. The optimal zone for sugar-formation ability ranged from p_H 5.0 to 5.5 and for starch disappearance from 4.0 to 6.0. A part of the amylase activity still remains at 0°. The value of the temp. coeff. of the ability to form sugar falls with increasing temp. The coeff. A of Arrhenius' temp. formula has a value of about 10,000 from 0 to 20°, of 9,400 from 20 to 30° and of 6,700 from 30 to 40°. The temp. coeff. for starch disappearance is rather const. between 20 and 40°. It is 9,600 from 20 to 30°, and 9,400 from 30 to 40°. Amylase in phosphate mixt. as buffer is the most stable towards heat at p_H 6.5 to 7.0, a somewhat more alk. soln. than that suitable for optimal activity. Inactivation of amylase at optimal p_H is slight on heating for 1 hr. at 35°. Heating at 55° for the same period destroys the activity. The inactivation is initiated at lower temps. and is more complete at other hydrión concns. The inactivation of the sugar-forming ability does not run a monomol. course. It is at first very rapid and then when it has reached a certain value it does not change. The inactivation of the

starch disappearance, however, is purely and simply a monomol. reaction. An alteration of enzyme concn. during heating has no effect on the inactivation. The phosphate concn. is also without effect. The value of the Arrhenius' temp. const. k_2 for the temp. coeff. A lies in the range from 35 to 55° between 11,000 and 80,000. It is very dependent on the hydrion concn. and reaches a max. at p_H 7.5. The lethal temp. at the optimal p_H is 45°. Amylase activity is not dependent on NaCl in low concns. It is slightly decreased in a 0.25% soln. and is more and more inhibited by higher concns. This refers to the disappearance of the starch reaction; for 1.0% NaCl soln. has no effect on the sugar-forming ability. Many tables give the details of the expts.

F. S. HAMMETT

Respiration of roots. J. STOKLASA. *Compt. rend.* 175, 995-7(1922); cf. *C. A.* 15, 248; 16, 3097, 3108.—Plants were grown in a nutritive soln. for 80 days, then transferred to sealed cylindrical vessels under sterilized conditions, the nutritive soln. being replenished with sterilized water. The tests were made at 20° to 22° and were of 18 to 20 days' duration. Through each vessel 20 liters of sterilized air was made to pass during 24 hrs., with or without radioactive treatment. The CO_2 respired in 24 hrs. per g. of dry root in 4 common grains and 4 common legumes without radioaction ranged from 74.6 mg. with *Hordeum distichum* to 119.8 with *Vicia faba*. With radioaction equiv. to 41.7 Mache Units, the CO_2 ranged from 124 mg. with *H. distichum* to 200.3 with *Pisum sativum*. Eleven common weeds were tested without radiations and the respired CO_2 ranged from 100.6 mg. with *Anthemis urvensis* to 270.1 with *Triticum repens*. Four of the weeds were subjected to radiations and the respiration was thereby increased about 50%. Only α -rays are active in increasing respiration. β -Rays hinder aerobic but promote anaerobic respiration; they intensify reductions while α -rays promote oxidations.

L. W. RIGGS

Protective power against salt injury of large root systems of wheat seedlings. W. F. GERICKE. *Botan. Gaz.* 74, 204-209(1922); cf. *Botan. Gaz.* 72, 404(1921).—It is shown that the relative physiol. values or growth efficiencies of different nutrient solns., and the tolerance of plants to salts, are affected by the extent of the root development of the test plants when placed in the media.

BENJAMIN HARROW

Effect of seeds upon hydrogen-ion concentration of solutions. W. RUDOLFS. *Botan. Gaz.* 74, 215-220(1922).—The H-ion concn. of solns. is markedly increased by contact with seeds.

BENJAMIN HARROW

The effect of hydrogen-ion concentration upon the growth of seedlings. L. W. TARR AND S. C. NOBLE. Univ. of Delaware Agr. Expt. Sta., *Bull.* 131, 52 pp.(1922).—Seedlings of wheat, corn and soy beans grown in a variety of nutrient solns. showed that the reaction of the soln. changed somewhat during growth. K H phthalate was used as a buffer to keep the reaction of the nutrient solns. const. throughout growth. Reaction adjustments were made by the use of NaOH or H_3PO_4 . It was shown in sep. expts. that phthalate was not toxic and that the amts. of NaOH or H_3PO_4 used to adjust the reaction were in all cases too small to be injurious. A reaction of p_H 3 was in all cases prohibitive of growth. Max. growth of wheat seedlings occurred at p_H 4 and greater concns. were harmful. Max. growth for both soy beans and corn was at p_H 5 and a value of p_H 4 was harmful. Each of the 3 seedlings showed no harmful results with decreased acidity until a value of p_H 6 was attained. At this point chlorosis appeared owing to the insoly. of Fe in all solns. having H-ion concns. less than p_H 6.

M. S. ANDERSON

Action of hexamethylenetetramine on the higher plants. E. NICOLAS AND G. NICOLAS. *Compt. rend.* 175, 836-8(1922).—Beans were germinated on wet blotting paper and the plants transplanted to a Knop culture soln. in such a manner that only the root was immersed in the soln. The vessels contg. the plants were surrounded by

black paper. From 0.1 to 1.5 g. of $(\text{CH}_3)_2\text{N}_4$ was added per l. of Knop soln. and the plants were grown from Apr. 6 to June 15, when the tops and roots were weighed. The addn. of $(\text{CH}_3)_2\text{N}_4$ in amts. from 0.1 to 0.25 g. per l. of culture soln. has a favorable effect on the growth of the bean plant. Beyond 0.25 or 0.3 g. its action is toxic and its toxicity is shown by a retardation in the digestion of the cotyledons. Its favorable action is seen in the largely increased number and size of the leaves. Beans grown in cultures free of N except N supplied by $(\text{CH}_3)_2\text{N}_4$ were able to use N in this form. Tereg (C. A. 14, 307) states that certain bacteria, fungi and mosses may utilize $(\text{CH}_3)_2\text{N}_4$, also that *Penicillium* and *Polytrichum* prefer it to NH_4NO_3 . L. W. RIGGS

Influence of copper salts on the yield of *Sterigmatocystis nigra*. MARIN MOLLIARD. *Compt. rend.* 175, 838–41 (1922).—With NH_4Cl as a source of N in the culture medium, 1 to 1500 represented the concn. of CuSO_4 that would prevent the growth of *S. nigra*. If the NH_4Cl is replaced by $(\text{NH}_4)_2\text{C}_2\text{H}_4\text{O}_6$, a concn. of 1 to 85 is necessary to prevent growth. In a culture free of Cu *S. nigra* consumed the sucrose in about 10 days, but with 1 to 3760 of CuSO_4 present, 30 days were required. In normal culture during the first 3 days CO_2 was evolved which corresponded to 0.413 of the sugar utilized. With CuSO_4 in the medium the CO_2 evolved in 6 days corresponded to 0.568 of the sugar used. L. W. RIGGS

Growth of plants in artificial light. R. B. HARVEY. *Botan. Gaz.* 74, 447–51 (1922).—H. has succeeded in raising a great variety of plants—wheat, oats, barley, rye, flax, buckwheat, white sweet clover, peas, beans, and lettuce—using artificial illumination entirely. Light was obtained from the N-filled tungsten filament (Mazda) lamps. The lamps were mounted on the ceiling of basement rooms about 5 ft. from the plants. Ordinary enamelled reflectors of the deep bowl type were used to throw the light downward. The lamps used were of the 200 watt and 1000 watt sizes.

BENJAMIN HARROW

The relation between the biological action of Röntgen rays and oxygen. EUGEN PETRY. *Wiener klin. Wochschr.* 35, 957–8 (1922); cf. C. A. 15, 3302; 16, 1971.—While raising the partial O pressure of the atm. and the presence of various oxidizing substances (Cl_2 , Br_2 , KMnO_4 , heavy metal salts, quinone, methylene blue, etc.) had no effect on the susceptibility of germinating seeds to the action of X-rays, on the other hand a preliminary treatment of the seeds with H_2O_2 had a profound effect on the susceptibility, especially in the root portion of seedlings, comparable to the previously reported effect of HCN. This reactivity of H_2O_2 and of HCN is ascribed by P. to the low mol. wt. of these compds. and to their great absorbability by the tissues.

W. A. PERLZWEIG

Influence of light on the formation of anthocyanin in the scales of lily bulbs. MARCEL MIRANDE. *Compt. rend.* 175, 496–8 (1922); cf. C. A. 17, 125.—The object was to learn the effects of variations in intensity and in refrangibility of light on the formation of anthocyanin. In direct sunlight the phenomenon is never observed as the scales wither rapidly without coloring. It is produced only in diffused light but not at all altitudes. Thus in a diffused light at an altitude of 2000 m. in a clear sky the pigmentation does not occur, but at an altitude of 300 m. pigmentation is rapid. Six light filters were made by stretching from 1 to 6 layers of white silk fabric over sheet iron frames. The amt. of light which passed these filters, estd. photometrically, was 0.53, 0.39, 0.22, 0.13, 0.089 and 0.07 for filters of 1 to 6 layers, resp. The lily scales were placed in saucers, covered with these light filters and the whole placed in direct sunshine in August. At an altitude of 300 m. there was no reddening under filter 1, slight under 2, and a max. under filter 3. At 600 m. the reddening began under filter 3 and reached a max. under filter 4. At 2000 m. reddening began under 3 and 4 but attained its max. under 6, which allowed only 0.07 of the direct radiation to pass. Scales placed in diffused light under

light filters of water, alum soln. or colored glass which arrested the ultra-violet, infra red and also the heat rays of the luminous portion of the spectrum were pigmented more rapidly than without these screens. At an altitude of 2000 m., scales exposed to diffused light were not pigmented, but if covered with a water or colored glass screen pigmentation took place. Ultra-violet rays oppose anthocyanic reddening. The only rays which produce reddening are those of the luminous portion of the spectrum. On filtering out differently colored rays by means of colored liquids or better by the Wratten monochromatic filters, rays with much narrower limits were tested with the result that wave lengths of 400-470 were most active. Lengths of 720 were much less active and green rays (538) were without action. The curve of pigmentation shows a max. in the red and a more important max. in the indigo and a min. in the green. L. W. R.

Sand down, a chlorosis of tobacco due to magnesium deficiency, and the relation of sulfates and chlorides of potassium to the disease. W. W. GARNER, J. E. McMURRAY, C. W. BACON AND E. G. MOSS. *J. Agr. Research* 23, 27-40(1923); see *C. A.* 17, 125. F. C. COOK

The course of absorption and the position of equilibrium in the intake of dyes by disks of plant tissue. G. M. REDFERN. *Ann. Botany* 36, 511-22(1922).—Disks of carrot, potato, artichoke and turnip were immersed in solns. of 0.005, 0.01, 0.05 and 0.1% strengths of neutral red, methylene blue, methyl violet, aniline blue, eosin and Congo red. Plant tissue which had been killed by immersing in a mixt. of dil. CH_3COOH and EtOH was used in a few tests. These results were practically identical with those where living tissues were used. The concn. of dye was estd. at intervals and the tissue was weighed. Methyl violet, neutral red and methylene blue gave similar results, all being rapidly absorbed, but aniline blue, another basic dye, was only slightly absorbed. Eosin, an acid dye, gave results similar to the aniline blue results. Congo red (acid) was not absorbed in appreciable amts. The absorption curves show a rapid rise at first, but gradually become horizontal as the condition of equil. is approached. This condition is reached more rapidly with concd. than with dil. solns. of dyes. The % absorption of the dye is increased with a decrease of temp. also as the external soln. becomes more dil. F. C. COOK

Moisture content of peach buds in relation to temperature evaluations. E. S. JOHNSTON. *Bolan. Gaz.* 74, 314-19(1922).—The expts., though limited in no., suggest a relationship between air temp. and the rate of increase in the moisture content of peach fruit buds. BENJAMIN HARROW

Specific acidity of water extract and oxalate content of foliage of African sorrel. G. P. WALTON. *Bolan. Gaz.* 74, 158-73(1922).—The advantages of detg. the sp. acidity (H^+ concn.) as well as the total (titrable) acidity of a water ext. of acid material are discussed. Only 2 compds. of oxalic acid, K binoxalate and Ca oxalate monohydrate, occur in the leaves of *Rumex abyssinicus* (an African sorrel). B. H.

Rest organs of water plants and hepatics. STARK. *Naturwissenschaften* 10, 875(1922).—This is a discussion of the recent work of Ringel-Süssenguth. The formation of winter rest organs in the H_2O plants, *Hydrocharis*, *Myriophyllum* and *Utricularia*, and the hepatics *Fegatella* and *Pellia* can be forced in summer by certain factors, such as low temps., quick temp. changes and absence of light, H_2O and nutrient salts. It is also possible to prevent their formation by favorable conditions or to cut short their life by certain means. Their life could not be shortened by treatment with Et_2O , but was effected by warm H_2O , KCN, and $\text{Al}_2(\text{SO}_4)_3$ baths, by injury and by opening of the bud. Conclusions: The beginning and duration of the rest period is dependent upon external chem. and phys. factors only, and is not an automatic, internal phenomenon. C. C. DAVIS

Carraheen (*Chondrus crispus*), III. The constitution of the cell wall. BARBARA

RUSSELL-WELLS. *Biochem. J.* 16, 578-86(1922); cf. Haas, *C. A.* 15, 3865.—Two exts. the "cold ext." (C. E.) and the "hot ext." (H. E.) were investigated. The former was obtained by first washing the hand-picked carrageen in running water, and then soaking for an hr. in distd. water. The aq. ext. was filtered and evapd., giving C. E. The weed was washed for several days in soaking water, and air-dried. This was heated on a water bath with fresh distd. water, and the filtrate evapd., giving H. E. The C. E. contains Ca and NH_4 ethereal sulfates, and its ash contains (besides sulfate and Ca) Mg, Na, K and traces of Fe. The ash of H. E. contains less Na and K and more Ca than C. E. Un-ionized Mg is present in both exts. The main oxidation products of both exts. contain mucic, oxalic and tartaric acids. Both exts. contain pentose radicals, but there are more in C. E. than in H. E. Cellulose is found in the residue left after extn. with hot water. Pectic bodies are absent from both exts.

BENJAMIN HARROW

Glutencasein from buckwheat. A. KIESEL. *Z. physiol. Chem.* 118, 301-3(1922).—Two protein preps. extd. from buckwheat with 0.1% HNaO soln. gave histidine 0.84,—; arginine 6.71, 7.55; lysine 1.66, 1.29%.

R. L. STRUBLE

The significance of mica minerals as a source of K for plants (GOLDSCHMIDT, JOHNSON) 15. Coloring matter of the fruit of *Gardenia florida* L (MUNESADA) 25. Photosynthesis and the possible utilization of solar energy (SPOHR) 13.

HAAS, P. and HILL, T. G.: Introduction to the Chemistry of Plant Products. Vol. II. Metabolic Processes. London: Longmans, Green & Co. 140 pp. 7s. 6d.

E—NUTRITION

PHILIP B. HAWK

NORMAL

The food requirements of children. III. Fat requirement. I. E. HOLT AND HELEN L. FALES. *Am. J. Diseases Children* 23, 471-80(1922); cf. *C. A.* 16, 3934.—The fat supply in the diet of infants at one year may be 4 g. per kg. body wt. At 6 yrs., it decreases to 3 g. per kg. and stays here for the rest of the growth period. IV. Carbohydrate requirement. *Ibid* 24, 44-55(1922).—The carbohydrate intake of more than 100 healthy children 1-18 years of age averaged 10 g. per kg. body wt. Of this 51% was sugar, including lactose, sucrose and fructose, and 49% was starch. It is regarded rational to allow in the diet of the child of av. activity about 12 g. carbohydrate per kg. body wt. at one year, decreasing the amt. to about 10 g. per kg. at 6 yrs. and maintaining it at this value throughout the remainder of the growth period. Too much carbohydrate is to be guarded against.

S. AMBERG

Food requirements in new born infants. A study of the spontaneous intake. H. K. FABER. *Am. J. Diseases Children* 24, 56-72(1922).—The demands of the infant for food, left to its own desire, exceed the basal requirements on the second day of its life, equal the av. total requirements of Benedict and Talbot (62 calories per kg.) on the third day, rise on the fifth day to the Heubner optimum of 100 calories and thereafter rise slowly to about 115 calories near the end of the second week.

S. AMBERG

Influence on carbohydrate metabolism of mineral waters. P. MAYER. *Deut. med. Wochschr.* 48, 827(1922).—Fermentation of 10% dextrose soln. with 100 g. yeast in 1 l. Karlsbad "Mühlbrunn" gave 45-46% alc. and 2.8-3.2% glycerol. The control with drinking water yielded 47.5-49% alc. and 1.8-2.1% glycerol. Mühlbrunn contains only 2 g. NaHCO_3 per l. With 50 g. Karlsbad salt contg. 38% NaHCO_3 the yield was 39% alc. and 10% glycerol with 75 g. salt, 33% alc. and 14% glycerol, against 48% alcohol and 2% glycerol in the controls.

S. AMBERG

The influence of the plane of nutrition on the maintenance requirement of cattle. A. G. HOGAN, W. D. SALMON AND H. D. FOX. Univ. of Missouri, Agr. Expt. Sta., *Research Bull.* No. 51, 48 pp. (1922). E. J. C.

The influence of subcutaneous injections of indole and skatole upon the nitrogenous metabolism of the rabbit. F. P. UNDERHILL AND ROBY. KAPINOW. *J. Biol. Chem.* 54, 717-20 (1922).—Two fasting rabbits received subcutaneous injections of 30 mg. of indole dissolved in Et_2O per kg. body wt. and 2 others received the same dose of skatole. The urine was analyzed for total N, creatinine, creatine, total S, inorg. and ethereal SO_4 . There were no noteworthy symptoms and the only apparent effect upon the urine was a slight increase in ethereal SO_4 after the administration of indole.

I. GREENWALD

Quantitative aspects of the role of vitamin B in nutrition. T. B. OSBORN AND L. B. MENDEL. *J. Biol. Chem.* 54, 739-52 (1922).—Rats of different ages, previously maintained on the normal mixed diet, were placed on a diet of casein 18, starch 54, lard 15, butter fat 9 and salt mixt. 4% (*C. A.* 13, 2063), *ad lib.*, with varying additions of dried yeast from a single lot of brewery yeast, when the rats had reached a weight of, approx., 40, 70, 150 or 240 g. Addition of 200 mg. dried yeast daily was adequate for all; 100 mg. was less satisfactory, particularly with rats weighing more than 200 g.; 50 mg. was still less satisfactory and 25 mg. failed to secure even maintenance of body wt. in the larger animals. Calcs. indicated that the daily requirement of that particular dried yeast was from 50 to 60 mg. per 100 g. of rat. It was apparently a little less than this in some of the larger animals, perhaps because of the increased amt. of adipose tissue. Similar results were obtained with a yeast concentrate. I. GREENWALD

Studies in inorganic metabolism. IV. The influence of yeast and butter fat upon magnesium and phosphorus assimilation. L. JEAN BOGERT AND RUTH K. TRAIL. *J. Biol. Chem.* 54, 753-61 (1922); cf. *C. A.* 17, 127-8.—In the 2 normal women in whom the addition of yeast favorably influenced the Ca balance, there was a similar favorable effect upon the Mg and P balances. The third subject showed an improvement in P balance but not in Ca or Mg balance. The substitution of an equal wt. of butter fat for the vegetable fat had a favorable effect on the Ca, Mg and P balance in all 4 subjects studied. I. GREENWALD

Vitamin A content of lard obtained from hogs on a control ration. MARGUERITE G. MALLON AND MARJORIE CLARK. *J. Biol. Chem.* 54, 763-6 (1922).—Lard was prepd. in the lab. from the back and leaves of hogs that had previously been fed for 12 weeks on yellow corn and clover pasture and for 11 weeks on yellow corn alone. This was then fed, as 30% of the ration, to 4 rats, all of which developed xerophthalmia. The control rats, receiving 5% of butter fat, instead of 5% of the lard, did not develop this condition. I. GREENWALD

A comparison of the Du Bois and the Harris and Benedict normal standards for the estimation of the basal metabolic rate. WALTER M. BOOTHBY AND IRENE SANDFORD. *J. Biol. Chem.* 54, 767-81 (1922).—The formulas of Harris and Benedict (*C. A.* 13, 1221, 1722) for calcg. basal metabolism from the body wt. in kg., height in cm., age in years and certain constants, may, by substituting 21 for number of years and Du Bois values for normal basal metabolism per sq. meter of surface at age 21 (*C. A.* 10, 2101), be converted into formulas for calcg. the surface area from the weight and height. Application of these formulas to subjects whose surface area had been measured by Benedict by his photographic method or by Du Bois by his mold method (*C. A.* 9, 1795) indicated that they were almost as accurate as that of Du Bois (*C. A.* 10, 1987) for the same purpose. These derived formulas fail in the case of infants and very short individuals. B. and S. applied their derived formulas to the heat prediction tables of Harris and Benedict for men and women between the heights of 151 and 200 cm. and

weights of 25 and 124 kg. and compared the results with those obtained by calcs. by the Du Bois formula. The differences were slightly less than $\pm 4\%$, except towards the limits of the Harris and Benedict tables, where it is reasonable to suppose, from the warning of these authors against the application of their formulas beyond the ranges given in the table, that these formulas and tables are least accurate. "Harris and Benedict, in their correlation formula, assume that a small subject will show more than twice the percentage decrease in heat production for advancing age than a large subject, while Du Bois assumes that age affects alike both small and large people. Harris and Benedict assume a reversed action for sex, depending on the size of the subject, by predicting first that large men have a greater heat production than similar sized women and second that small women have a greater heat production than small men." B. and S. regard both of these assumptions as unsupported by the evidence available. "The Du Bois formula for the determination of the surface area and the Du Bois normal standards of heat production for each sq. m. of body surface for age and sex are considered by us the best method at present available for predicting the normal heat production." Cf. following abstr.

I. GREENWALD

Summary of the basal metabolism data on 8614 subjects with special reference to the normal standards for the estimation of the basal metabolic rate. WALTER M. BOOTHBY AND IRENE SANDIFORD. *J. Biol. Chem.* 54, 783-803(1922); cf. preceding abstr.—In 127 normal subjects, the observed values for the basal metabolism differed from those calcd. from the Du Bois formulas, by from -15 to -11% in 3.2%, by from -10 to $+10\%$ in 92.1%, by from $+11$ to $+15\%$ in 4.0% and from $+16$ to $+20\%$ in 0.7%, of the total number. In 2417 cases, in which there was no evidence of thyroid involvement, and including the 127 normals, the distribution was below -20% , 2.1%; -20 to -16% , 2.2%; -15 to -11% , 4.6%; -10 to $+10\%$, 77.1%; $+11$ to $+15\%$, 8.3%; $+16$ to $+20\%$, 3.1%. Data are also presented for 6197 patients with thyroid involvement, for which it is stated that 90% showed typical increases or decreases in basal metabolism according as the clinical condition indicated hyper- or hypothyroidism. In addition, there were 87 patients, in whom a positive diagnosis of hyperthyroidism was not reached. Two of these had metabolic rates from -15 to -11% , 31 from -10 to $+10\%$, 35 from $+11$ to $+20\%$ and 19 above $+20\%$. The large number of high rates may be due to the fact that about 0.5 of the patients had but one detn. performed. In 102 normal persons, more than 21 yrs. old, the surface area calcd. by the Du Bois formula and that calcd. by the formulas derived from those of Harris and Benedict differed, in most cases, by less than 1% and in only 1 instance by as much as 5%, the av. for the entire group being 1.69 sq. m. by the former method and 1.68 sq. m. by the latter. The deviation in the metabolic rate is from -10 to $+15\%$, av. $+0.6\%$ from the Du Bois standard and from -8 to $+21\%$, av. $+4.8\%$ from the Harris and Benedict standards. Similar results were obtained in 249 cases of chronic nervous exhaustion, 29 of migraine and 73 of obesity. "The basal metabolic rates, as calcd. by the Du Bois method, are more often -5 and $+5\%$, between -10 and $+10\%$ and between -15 and $+15\%$ than by the Harris and Benedict method. Possibly the absolute level of the Du Bois age and sex standards is slightly too high; however, at the present time there are not sufficient data to warrant their alteration."

I. GREENWALD

The nutritional requirements of mental work. OTTO KESTNER AND H. W. KNIPFING. *Klin. Wochschr.* 1, 1353-4(1922).—Metabolism expts. conducted with a Benedict respiratory app. on a series of quiescent students showed that the O consumption and the CO₂ elimination were increased very little by mental work. There was, however, a change in the respiratory quotient. In one case the quotient was 0.91 when resting, 0.93 during the first period of mental work and 0.80 during the subsequent period. Some acid must have been produced that reduced the CO₂-carrying capacity of the blood.

The mental effort markedly increased the concn. of the H_2PO_4 in the blood. This reduction in the alkaline reserve supply of the blood can be compensated for by eating foods that will not only stimulate the secretion of gastric juice, but that will combine with the acid so secreted, thereby producing an alkaline tide in the blood. Meat is recommended as a most efficient diet for those engaged in mental work.

MILTON HANKE

The problem of artificial nourishment. RIETSCHEL. *Klin. Wochschr.* 1, 1393-5 (1922).—A review.

MILTON HANKE

The significance of various vitamins for iron assimilation in growing individuals and the composition of the body ash after vitamin-free and vitamin-containing feedings. S. YOSHUE. *Biochem. Z.* 134, 363-74(1922).—Young mice were fed various diets. The general conclusions are that the ash content of the individual animal body increases when the vitamins are withheld. The most marked effect is shown in complete avitaminosis; the next when the A factor is given; next when C is fed; then those with factor B; and finally the normal animals with the least ash content as based on body wt. The Ca, Mg and apparently the P content of the body ran parallel with the total ash values. Fe, K and NaCl also pursued a parallel course, but opposite to the curve for the Ca, Mg and P; *e. g.*, those which had the most Ca showed the least K, etc. The vitamins of rice bran and kohl-rabi seemed to be better for a Fe maintenance than were those of butter. The presence of all vitamins was of course the most favorable. The decrease in KCl and NaCl of the body in total or partial avitaminosis is apparently due to disintegration of the soft parts. The feeble Fe retention when much Fe was fed appears to be a direct disturbance of Fe assimilation in certain organs, because of the lack of vitamin. The relative increase in total ash of Ca, Mg and P in avitaminoses is apparently due to the greater resistance of the skeleton.

F. S. HAMMETT

The influence of function on the course of avitaminosis. S. YOSHUE. *Biochem. Z.* 134, 375-80(1922).—Rats were maintained on vitamin-contg. and vitamin-free diets. Some were exercised and others were not. Studies were made of the duration of life and of serial sections of the spinal cord. The results showed that avitaminosis brought about severe functional disturbances in the central and peripheral nervous system as in other organs so that the exercised rats, without any particular appearance of muscular paralysis, died sooner than the others. Hence avitaminosis is considered as laying the foundation for the development of damage to the organism when stress is put upon it.

F. S. HAMMETT

Carbohydrate metabolism in avitaminosis. I. Blood sugar. J. A. COLLAZO. *Biochem. Z.* 134, 194-214(1922).—The blood-sugar concn. in avitaminosis is like that in partial starvation. Hence avitaminosis is a kind of undernutrition. Further speculations are to the effect that the vitamins are sp. stimulants for the trophic regulation of cellular assimilation.

F. S. HAMMETT

Vitamin underfeeding. W. CRAMER. *Brit. J. Exptl. Pathol.* 3, 298-306(1922).—Observations have been made on a stock of rats which have been kept through many generations on a natural diet, the vitamin content of which, though restricted, was adequate to enable them to grow and breed and to prevent the occurrence of obvious ill-health. A comparison of rats from these stocks with animals from a stock fed on the same diet supplemented with an abundant supply of vitamin shows that there is such a condition as "vitamin underfeeding" and that it may occur on a natural diet. Such vitamin underfeeding does not lead to any obvious ill-health; the animals are in appearance normal, healthy animals. But vitamin underfeeding, especially if it has occurred in infancy, impresses itself upon the organism as a lasting weakness which only manifests itself when the organism is exposed to a strain. Hence the importance of insuring an abundant supply of vitamins in the food, especially to the pregnant and lac-

tating mother and to the growing child. The fact that vitamins have a positive, stimulating drug-like action and thus act as food hormones is put forward to replace the present conception of their mode of action. These conclusions open up a social aspect of the vitamin problem which has hitherto not been recognized, but which is at least as important as the actual production of diseases by a severe vitamin deficiency. They suggest that the physical make-up of a community is detd. largely by the ease and regularity with which an abundant supply of vitamins is secured to the pregnant and nursing mother and to the growing child.

HARRIET F. HOLMES

Anatomical investigation on the question of the accessory food substances. ALBERT MEYERSTEIN. *Arch. path. Anat.* (Virchow's) 239, 350-62(1922).—The sex organs suffer especially in the event of a deficient vitamin supply. The cells are poorly developed and fail in normal maturation, and the interstitial tissue is relatively increased. Attention is called in this connection to the relationship between the sex glands and body growth.

E. R. LONG

The effect of radiation with the mercury-vapor quartz lamp on the growth of rats fed on a diet deficient in vitamin A. E. MARGARET HUME. *Lancet* 1922, II, 1318-21.—Irradiation with the Hg-vapor quartz lamp can prolong the growth of rats on a diet free or almost free from vitamin A. Whereas without irradiation growth ceased to be normal after 7-10 days. With irradiation it continued normal for 35-50 days. Symptoms of vitamin A deficiency then set in. Attempts to relieve symptoms of vitamin deficiency by irradiation of animals which had long (over 90 days) been on a deficient diet failed. It is concluded that there is an interaction of light and vitamin A in the growth of rats, but no photosynthesis of the vitamin. The vitamin is economized or the vitamin stores are forced to yield it up at a rate sufficient to produce normal growth until they are wholly exhausted.

E. R. LONG

The effect of radiation with the mercury-vapor quartz lamp on the growth of rats on a diet deficient in the fat-soluble growth-promoting factor. H. GOLDBLATT AND K. M. SOAMES. *Lancet* 1922, II, 1321-4.—For 4-5 wks. after being placed on a diet deficient in the fat-sol. vitamin rats radiated with the Hg-vapor quartz lamp grow at the normal rate. Slight but temporary improvement is noted on radiating rats which have ceased to grow as a result of fat-sol. vitamin deficiency. Radiation is thus no substitute for the vitamin but in some way economizes it in its action.

E. R. LONG

The changes in the para-ocular glands which follow the administration of diets low in fat-soluble A; with notes of the effect of the same diets on the salivary glands and the mucosa of the larynx and trachea. SHINNOSUKE MORI. *Bull. Johns Hopkins Hosp.* 33, 357-9(1922).—Histological evidence in rats indicates a marked diminution or practical cessation of secretion on the part of the lacrimal, salivary, and other secretory glands. For the changes occurring in the para-ocular glands see C. A. 16, 2888.

A. P. LOTHIROP

The constancy of the creatine-creatinine excretion in children on a high protein diet. V. J. HARDING AND O. H. GAEBLER. *J. Biol. Chem.* 54, 579-87(1922).—"Normal children, of the same age and under the same environment, excrete the same quantity of total creatine (creatinine + creatine expressed as creatine). If the total creatine in mg. be expressed as a coeff. of the body wt. in kg., the figure obtained is a const., independent of the age of the child, and of the same magnitude as the creatinine coeff. of an adult man." The creatinine coeff. rises definitely with increasing age and wt. as there is an increasing % of musculature and 16 years is an av. age at which creatinuria disappears even upon a high protein diet. At this age the musculature has attained its max. development in relation to body wt. "These findings receive their simplest interpretation by assuming that creatine is produced from protein either *in toto* or from a special fraction of it, is stored in the muscles, and is converted into creatinine.* With

the satn. of the muscles with creatine, any excess production will find its way into the urine, and provided the dietary protein is not reduced to such a low level that a condition of protein starvation occurs, the urinary creatine will appear as a waste product of exogenous origin. However, the creatine production reaches a max. and once that max. is reached no amt. of further feeding of protein, however excessive, will result in augmented creatinuria. Similarly, moderate decreases in protein may fail to lower or abolish an existing creatinuria. The muscular system does not control the production of creatine as a child of 3 produces as much total creatine as an adult man. Creatine disappears from the urine of the adult man when the creatinine coefficient has attained its av. max. value, and the muscular system has also reached its av. adult % of the total body wt." In general creatinuria in pathol. conditions (hyperthyroidism, acromegaly, muscular dystrophy) shows the same general rule as creatinuria in children provided the diet is high in protein.

A. P. LOTHROP

The increase in autoprotoeolytic activity and the production of amino acids in the liver during inanition; its relation to the endogenous origin of amino acids in the blood. H. DELAUNAY. *Compt. rend. soc. biol.* **87**, 1091-3(1922).—Autolysis expts. were performed under strictly aseptic conditions with various organs of dogs either after a meat meal or after 48 hrs. of fasting in which the non-protein N and protein N were detd., and of the former also the amt. represented by the amino acids. In the liver 60-70% of the non-protein N is in the form of amino acids whereas in all other tissues only 40-50%. D. ascribes, therefore, to the liver a particularly great role in the matter of amino-acid production, and this leads him to believe that the liver exercises the same function in the metabolism of protein as it does in the carbohydrate metabolism. S. MORAVULTS

Ocular manifestations of the rat which result from deficiency of vitamin A in the diet. A. M. YUDKIN. *J. Am. Med. Assoc.* **79**, 2206-8(1922).—Expts. on rats with various diets deficient in vitamin A showed that the incipient changes in the eyes are like xerosis of the conjunctiva and cornea in man, and the more advanced picture is that of keratomalacia.

L. W. RIGGS

Vitamins in ice cream. A. H. SMITH. *J. Am. Med. Assoc.* **79**, 2221-2(1922).—Ice cream was tested before and after freezing for vitamins A and B by the technic of Ferry. For the antiscorbutic vitamins the procedure of Sherman, Lamar and Campbell was followed, with the following ration: soy-bean meal (autoclaved) 83%, filter paper pulp 3, cod liver oil 5, dried yeast 3, Ca lactate 3, and NaCl 3. Plain vanilla ice cream contg. 10% butter fat was used throughout the expts. Rats with ophthalmia on a diet low in vitamin A were cured and normal growth was resumed by 1 g. daily of either frozen or unfrozen ice cream. Growth was not obtained with 0.25 g. of the ice cream daily, until the eyes were entirely clear, and then only at a sub-normal rate. Vitamin B of the ice cream can be accounted for by the equiv. quantity of milk used in it. Freezing has no effect on vitamin A or B. Ice cream made from pasteurized materials contained no significant amt. of vitamin C.

L. W. RIGGS

Absorption of pepsin and of hydrochloric acid by foods. JEAN EFFRONT. *Compt. rend.* **175**, 799-803(1922); cf. *C. A.* **16**, 1257.—Peeled fruits, salads and other raw foods were pressed, the press cake was washed with water, collected on a sieve and again pressed. In the pulp thus obtained the dry matter, ash, alky. of the ash and phosphates of the ash were detd. Legumes were first boiled 2 hrs. and then treated as above. For each test 20 cc. of the pulp and 40 cc. of a 1 or a 0.5 per 1000 soln. of pepsin were used. This mixt. was kept in flasks at 37° for 2 hrs., then the liquid portion was passed through filters deprived of absorbing power. Controls with pepsin and water were run. The pepsin was detd. in the filtrate by the Fuld method slightly modified. One unit of pepsin is that quantity of active substance capable of transforming 1 mg. of edestin in 30 min. at 20°. In 12 tests the power per g. of dry substance to absorb pepsin ranged

from 20.7 units by raw tomato to 1303 units by unripe prunes. Ripe fruit absorbs much less pepsin than unripe fruit. With melons, lettuce and salads the reaction of the medium was without influence upon the absorption, but with cabbage, cauliflower, turnip, endive and carrot, the absorption of pepsin increases with the acidity. To det. the absorption of free acid, 40 g. of pulp of known water content was dild. with 120 cc. HCl, 2.5 in 1000, and the mixt. was placed in the thermostat at 37° for 2 hrs. Absorption of HCl in mg. per 100 g. of dry matter ranged from 752 with apple pulp to 3900 with cauliflower pulp. The alky. of the ash of the pulps expressed in mg. HCl per 100 g. of dry matter ranged from 520 in cauliflower to 2580 in lettuce and appeared to bear no relation to the absorption of acid. In prescribing a diet the absorptive powers of the foods upon pepsin and HCl should be considered both from the point of view of peptic digestion and of disinfection of the digestive tube.

L. W. RIGGS

Supplementary food substances. Effect of fat and cholesterol-deficient feeding upon the growing organism. PH. NIEMES AND LEONH. WACKER. *Arch. expl. Path. Pharm.* 93, 241-68(1922).—Rats were fed various diets, skim milk and whole milk, with and without cholesterol. A diet of skim milk and starch prevents the growth of young rats and leads to death, but rats almost fully grown can subsist on this diet for fully a half a year. With the younger animals the intensity of the disturbance was proportional to the age of the rats, the younger the rat when the diet was commenced the more quickly death occurred. Rats of similar ages fed upon whole milk and starch remained alive and gained in wt. At the time of death the rats upon the skim milk were emaciated and without fat deposition, and a similar condition was noted in animals which had received the same diet with the addition of cholesterol. The addition of the cholesterol hastened rather than retarded death. When gray-black rats were fed skim milk and starch for 5 mo. they became brown in color, but their normal color was restored when they were returned to a normal diet. The deficient diet caused the rats to become spastic and to show kyphosis of the thoracic vertebrae. A marked gas formation in stomach and intestines was noted at the necropsy of the skim milk animals; this was almost entirely lacking in those fed upon whole milk, with or without cholesterol. The whole milk rats were more resistant to infections than were the skim milk animals. In the young control animals upon whole milk the addition of cholesterol to the diet did not stimulate growth.

G. H. S.

Organic foodstuffs with specific action. XIII. Deficient oxygen supply of the cells as cause of the appearance of alimentary distrophy in pigeons. EMIL ABDERHALDEN AND ERNST WERTHEIMER. *Arch. ges. Physiol. (Pflüger's)* 194, 647-73(1922); *Chem. Zentr.* 93, 632.—Normally fed pigeons are more resistant to the lack of O than those fed exclusively on polished rice for some time. The latter do not appear to be more susceptible to HCN poisoning than normally fed pigeons of the same age and wt. Active exts. of brewer's yeast have no influence upon cyanogen or HCN poisoning. Cf. *C. A.* 16, 2888.

H. L. DURAND

Organic foodstuffs with specific action. XIV. EMIL ABDERHALDEN AND ERNST GÜLLHORN. *Arch. ges. Physiol. (Pflüger's)* 195, 1-21(1922); cf. preceding abstr.—The effects of a series of yeast exts. of diff. types were detd. upon frog musculature—gastrocnemius, esophagus, and heart. Certain exts. caused a simple paralyzing action, negatively inotropic; others, in suitable concns., increased the efficiency of striated, non-striated, and heart muscle. Reactions brought about by such compds. can be induced by completely protein-free exts. XV. EMIL ABDERHALDEN. *Ibid* 199-226.—A synthetically prepd. food contg. amino acids, mineral salts, and water was fed mice and rats. For a short time they could be maintained in normal equil. but later the lack of nutramines became obvious. This lack was readily met by the addn. of yeasts, butter, and some other substances. By utilizing such a foodstuff the relative significance

of the amino acids was detd. It was found that *l*-tryptophan is essential, its lack leading to severe disturbances. Likewise, *l*-cystine is indispensable, and probably plays a role in growth. *l*-Tyrosine and *l*-phenylalanine can be replaced by other substances but lysine and arginine cannot. Histidine is essential. The leucines can be replaced, but if asparagine and glutamic acid are lacking there is a loss in body wt. Glycocoll, alanine and hydroxyglutamic acid are not indispensable. The absence of the purine or pyrimidine bases or of cholesterol was not reflected in any change. XVI. Comparison of the action of heated and unheated bran and yeast and of the organs of normally nourished pigeons with those of pigeons fed upon polished rice. E. ABDERHALDEN. *Ibid* 432-59.—Detailed protocols showing the changes in body wt. of pigeons fed on the diets indicated are presented. Bran or yeast when heated fails in large measure to protect against polyneuritis. XVII. E. ABDERHALDEN AND E. WERTHEIMER. *Ibid* 460-79.—Pigeons which had been fed upon a polished rice diet were more susceptible to intoxication by increased CO₂ in the air than were normal pigeons. Considerable differences in gas metabolism were also noted. When exposed to irradiation the dystrophy pigeon reacts in a transitory manner with an increase in gas metabolism and an elevation of temp. Both the normal and the deficient diet pigeons react to adrenaline with a fall in body temp., but animals fed upon rice are much more susceptible to its action. When fed benzoic acid the normal animal revealed ornithuric acid in the intestinal tract while the dystrophy animal showed none. In the late stages of dystrophy the action of the heart is retarded. XVIII. *Ibid* 480-6.—Mixed diets of known compn. made up from chem. pure food constituents fed to pigeons led to the same results as are obtained by feeding polished rice. G. H. S.

Creatine intolerance of infants. H. BEUMER. *Z. Kinderheilk.* 31, 236-46 (1922).—Creatine was administered to infants by mouth and by intravenous injection. Detns. of the creatine elimination led to the conclusion that an intolerance to exogenous creatine is a peculiar characteristic of infant metabolism. G. H. S.

Tryptophan requirements of children. TOSHIO IBE. *Z. Kinderheilk.* 31, 257-89 (1921).—The tryptophan requirements, optimum and minimal, of children of different ages were detd. In the new born the optimum amt. is 0.05 to 0.08 g. per kg.; the optimum amt. increases with age up to 2 yrs. (optimum amt. 0.09 to 0.1 g.); and from this time decreases with age, so that at the age of 13 to 15 yrs. the values are 0.04 to 0.055 g. Colostrum contains a much higher percentage of tryptophan than does the later milk. G. H. S.

Blood chlorine and digestion, with particular reference to ingestion of foods rich in fats. ADOLF SALOMON. *Z. Kinderheilk.* 32, 271-81(1922).—The observations of Scheer and Boenheim, namely, that the amt. of Cl in the blood is associated with the ingestion of food and is decreased during gastric digestion, are confirmed. An exception to the rule is that such a diminution of blood Cl does not take place when the ingested food has a high content in fat. G. H. S.

Significance of the type of solution or degree of subdivision of organic foodstuffs in infant feeding (crystalloids, colloids, suspensions, emulsions). J. ROSENBERG AND LAUTER. *Z. Kinderheilk.* 32, 316-21(1922).—Data indicate that the physical state of ingested food is as significant, or more important than the chem. compn. in governing the effect produced by the food within the intestinal tract. G. H. S.

Experimental investigations concerning the influence of vitamins on digestion and food assimilation: The theory of vitamin activity. A. BICKEL. *Klin. Wochschr.* 1, 110-2(1922).—A dog with a Pavlov pouch was fed a vitamin-deficient diet consisting of polished rice, pure wheat protein, salt and lard. This diet did not call forth a secretion of gastric juice in the Pavlov pouch. When, however, a small amt. of dil. alc. was added to the diet, a normal secretion of gastric juice was invariably obtained over a

trial period of 70 days. The vitamin-deficient nourishment does not interfere with the secretory power of the gastric glands; the diet merely fails to act as a gland stimulant. A metabolism expt. was carried out on an 11-kg. dog to ascertain if the lack of vitamins interfered with the absorption of the fully digested food. The dog was kept for 20 days on a diet consisting of 50 g. horsemeat, 25 g. butter, 50 g. polished rice, 3 g. salt and 700 cc. of water. The animal's weight was unchanged. He excreted an av. of 5.4 g. dry feces per day with a N content of 0.18983 g. The diet was then changed to one consisting of 44 g. wheat protein, 20 g. lard, 60 g. polished rice, 3 g. salt and 700 cc. of water. This diet has a calorific value equal to that of diet 1, a N content slightly greater than that of diet 1, and practically no vitamins. During a trial period of 107 days, which was terminated by death, the animal lost 3.9 kg. in wt. and excreted an av. of 4.9 g. dry feces per day with a N content of 0.1128 g. The rate of absorption of the digested vitamin-deficient diet was normal. Nitrogen equil. was maintained for the first 52 days; but there was a loss in wt. of 2 kg. Body fat and carbohydrates must have been sacrificed during this period. After the 52nd day, the nitrogen balance became rapidly negative, was most strongly negative on the 69th day, then became slowly less negative so that on the 97th day there was in fact a marked N retention, which continued up to the 107th day, when the animal died in N equil. Of the 3.9 kg. body wt. lost, only 0.911 g. consisted of protein; hence by far the largest part of the body consumed consisted of fats and carbohydrates. In spite of this increased loss of body fats and carbohydrates, there was a decrease in the amt. of oxygen consumed; hence unusual, incompletely oxidized end products of the carbohydrates and fats may have been excreted. Vitamins do not influence either the digestion or the absorption of food materials. In the absence of vitamins the body cells gradually lose their ability to resynthesize and store the circulating food digestion products; so the animal must sacrifice its own tissue. M. H.

ABNORMAL

Study in basal metabolism in dementia precox and manic-depressive psychoses. CHAS. E. GIBBS AND DORETHERA LEMCKE. *Arch. Intern. Med.* 31, 102-15 (1923).—In 37 detns. in 14 cases of manic-depression, the basal metabolism varied from -15 to $+7\%$, and the av., for an individual, from -12 to $+6\%$. One other patient gave $+34$ and $+20\%$. In 19 detns. on 9 patients with dementia precox, the results were from -27 to -6% . In 2 others, one of whom was uneasy during the detn. and the other of whom was examined at a time when he was subject to periods of excitement and overactivity, the values were $+12$ and an av. of $+15\%$, resp. Although several of the dementia precox patients did show some evidence of disturbed growth, including incomplete sex maturity, the findings could not be explained satisfactorily in terms of thyroid or pituitary disorder. Thyroid by mouth raised the rate to normal in 2 cases of manic-depressive depression, but did not in a case with more marked constitutional psychopathic features. There was no immediate mental improvement. I. G.

Metabolic disturbances in cats on a milk diet. GEO. W. PUCHER AND K. F. CORI. *J. Biol. Chem.* 54, 567-78 (1922).—"Cats when fed on meat and H_2O excrete a urine normal for carnivorous animals. The total CO_2 content of the urine is very small and const. in value (0.018 g.). Cats when fed on milk (150-300 cc.) excrete within 24 hrs. a urine which shows the following characteristics: alk. to brilliant yellow or even to phenolphthalein; substances which easily reduce Benedict's soln. (5 min. boiling); huge amts. of bicarbonates (calcd. from the total CO_2 evolved); and increase of the NH_3 and the NH_3 -total N ratio. These symptoms were observed as long as the animals were maintained on a milk diet (3 weeks). Within 48 hrs. after the withdrawal of the milk the animals returned to normal. Milk sugar is not responsible for these changes in the alk. metabolism of the cats." The nature of the reducing substance will be detd.

later; it was not lactose. The mechanism of these changes in the metabolism or the substances present in the milk which induce them have not been completely detd. It is the intention of the authors to det. these points and to apply, if possible, their observations to metabolic disturbances produced in infants by cow milk. A. P. L.

Elimination of acetone bodies in a prolonged fast. MARCEL LABBÉ AND F. NEPVEUX. *Compt. rend. soc. biol.* 87, 602-5(1922).—The subject fasted the first 3 days without H₂O; from the 4th to the 15th day he received H₂O; from the 15th to the 31st day he was given lemonade with an av. content of 22 g. of carbohydrate per day; in the remaining 11 days of his 41-day fast he again had only plain H₂O. During this prolonged fast the daily detn. of the acetone bodies and org. acids (by the method of Van Slyke) shows a rapid increase with the onset of the fast and from a normal acetone body excretion of 0.061-0.093 g. per day it quickly rose to a max. of 6.241 g. on the 7th fast day when it commenced to fall again. During the lemonade period the acidity and the total acetone excretion diminished very markedly: from 1.381 g. on the 15th it dropped to 0.067 g. on the 31st day. The urinary acidity, the NH₃ elimination and the org. acids all behaved in the same way. When, in the last period, the subject was once more on water the acetone bodies, etc., again increased in the daily urine but it no longer reached the high level observed in the pre-lemonade period. The organism thus seems to adapt itself to the biochem. conditions existing in the organism under fasting. S. MORCULIS

A study of acidosis in prolonged fasting. MARCEL LABBÉ AND F. NEPVEUX. *Compt. rend. soc. biol.* 87, 605-7(1922).—The elimination of NH₃ N does not follow closely that of the acetone bodies, and is in no relation to the β -hydroxybutyric excretion. The NH₃ N in this subject never reached as high values as in Cathcart's subject. The amino-acid N diminished gradually and continuously during the fast but its changes were not related in any way to the acetone excretion. The total acidity curve ran parallel to the acetone bodies in the urine and was greatly decreased under the influence of the lemonade with a daily av. content of 22 g. carbohydrate during the lemonade period. The org. acids studied by Van Slyke and Palmer's method follow the curve of the urinary acetone bodies but their amt. is much smaller than in the case of diabetics. There was no glucosuria, and the authors could not substantiate the view of Ambard that the appearance of acidosis is associated with a lowering of the blood sugar level. Conclusion: The acidosis of fasting is strictly a ketosis while the diabetic acidosis is associated with an increased elimination of org. acids and with a distinct increase of NH₃ and amino acid in the urine. S. MORCULIS

Balancing the diabetic diet. SOLOMON STROUSE. *J. Am. Med. Assoc.* 79, 1899-1900(1922).—As a working basis for balancing diabetic rations it is assumed that the basal caloric requirements should be met, the N balance be maintained and the ratio of fat to glucose must be kept below the point at which a clinically significant ketosis appears. Reasoning from the recent (1921-2) work of Shaffer, Newburgh, Woodyatt, Wilder and others the diet may be balanced by the following simple procedure: Protein should be equal to 0.66 g. per kg. of body wt. Carbohydrate should be equal to the glucose tolerance minus 58% of the protein. Fat should furnish enough cal. to equal the basal caloric needs minus the cal. supplied by the protein and carbohydrate. The amt. of fat must be within limits which will prevent the development of ketonuria and equals 2.5 to 4.0 g. of fat for 1 g. of available carbohydrate. L. W. RIGGS

Diabetes, β -hydroxybutyric acid and levulose. A. DESGREZ, H. BERRY AND F. RATHERY. *Compt. rend.* 175, 536-9(1922).—The various sugars are not indifferently interchangeable in the ration. The equil. of the living organism is in a certain degree conditioned by the mol. structure of the food. It has become necessary to consider alimentary specificity in the chemical sense of the term. The ingestion of levulose

helps to correct some of the accidents of metabolism. Its use in the diabetic in general furnishes a means of forestalling and combating the elimination of β -hydroxybutyric acid. The carbohydrate tolerance of a diabetic being known, it suffices to add to the ration of phosphate and vitamin B, levulose equiv. to the max. amt. of carbohydrate which the patient is able to assimilate.

L. W. RIGGS

Avitaminosis and starvation. E. F. TERROINE AND H. BARTHELEMY. *Compt. rend.* 175, 721-4(1922).—Expts. were made with mice and widow birds (*Vidua principalis*). One series of 7 mice and 8 birds received only water. The second series of 15 mice received bread while the 9 birds of this series were fed millet seed. Both rations were subjected to a temp. of 125° for 30 min. The fats and lipoids were estd. according to the method of Kumagawa. In starvation the fats and lipoids of the mice at death ranged from 22.3 to 26.2, av. 23.6 g. per kg. of animal; for the birds the range was 22.2 to 26.0, av. 24.35. In vitamin deficiency at death the fats and lipoids ranged from 23.9 to 35.7, av. 29.0 g. in the mice and 18.8 to 31.2, av. 24.7 g. in the birds. But in the second series the animals during the latter days of the period were subject to the nervous complications due to deficiencies in the diet which caused them to refuse food, whereupon starvation was added to deficiency disease. A comparison was therefore made of the fats and lipoids per 100 g. dry matter in the pectoral muscle of pigeons in the normal condition, dead from starvation, and killed at the appearance of symptoms of deficiency disease. The fats and lipoids in starvation were less than one-half the normal figure, while the appearance of deficiency symptoms occurred when there was more than the normal amt. of fats and lipoids present.

L. W. RIGGS

Hypogalactia. I. Qualitative hypogalactia. Effect of war diets upon the composition of mother's milk. RICHARD LEDERER. *Z. Kinderheilk.* 31, 141-9(1922).—The hypogalactia associated with war diets or with inadequate food is characterized by qual. changes in the milk, such as a lack of sugar, a deficiency of fat, and in individual cases a marked lack in the total N. II. Effect of hypogalactia on infants. *Ibid* 150-7.—The disturbances seen in infants fed upon the milk of mothers with hypogalactia are not to be ascribed primarily to a lack of food value in the milk, but rather to a constitutional irritability of the stomach and intestine of the infant, so that it reacts strongly to the effects of inanition.

H. G. S.

F—PHYSIOLOGY

ANDREW HUNTER

The presence of formic acid in the urine of infants and older children. M. MCNEAL AND CH. J. ELDRIDGE. *Am. J. Diseases Children* 23, 419-22(1922).—The Autenrich method for the detn. of HCOOH was used, with distn. after addition of H_2PO_4 to urine without a current of steam. In the distillate the HCOOH was detd. in the usual way by reduction of $HgCl_2$ to $HgCl$. This method gave results agreeing fairly well with those obtained by an Et_3O extn. method. The results indicate that urine of children contains HCOOH.

S. AMBERG

The proteolytic power of pancreatic juice with special regard to the action of calcium chloride. S. RACCHUSA. *Biochim. terap. sper.* 9, 261-6(1922).—The substrates used were casein, peptone, and freshly coagulated egg albumin. In the last case, addn. of 0.1 g. $CaCl_2$ to 5 cc. of pancreatic juice accelerated the digestion. The reverse effect was observed with casein and peptone.

H. W. BANKS, 3RD.

The effects of removal of the thymus. G. PIGHINI. *Biochim. terap. sper.* 9, 207-19(1922).—Removal of the thymus affects various parts of the system in approx. the following order of importance: osseous system, chromaffin, nervous-muscular, blood and serum, sex glands (male) (female), pancreas and liver, thyroid, hypophysis. The "thy-

mus greatly affects the Ca metabolism. Sub-normal ossification after its removal is probably not due to the development of acidity, but rather to lack of some sp. substances (hormones, enzymes) in the circulatory system. H. W. BANKS, 3RD.

Investigations concerning the theory of muscular contraction being due to the formation of acid. F. VERZÁR. *Arch. néerland. physiol.* 7, 68-75(1922).—The acidity produced in the muscle by tetanic contraction is far too small to account for the contraction. According to Burridge (*C. A.* 5, 1622) and Verzár, Bögel and Szányi (*C. A.* 17, 303) a p_H of about 2 or 3 is required to produce any appreciable contraction of the muscle fiber. In the muscle, however, after vigorous contractions no p_H lower than 6 is ever observed. In most cases it amounts to 6.8-7.0. With microscopic observation no place can be found in the muscle exhibiting a change of color. Furthermore, it must be considered that if the muscle is contracted by addn. of acid no tension is generated, as in the case of natural contraction. It is found that the work done by the muscle, contracted by acid, is never nearly as large as the work done by living muscles. Conclusion: The formation of acid may account for the *rigor mortis* but never for muscular contraction. R. BRUTNER

The surface tension of normal human blood. R. BRINKMAN. *Arch. néerland. physiol.* 7, 258-62(1922).—The surface tension of oxalate blood, drawn from the tip of human fingers, is detd. by the micromethod of Brinkman and van Dam. The values obtained for 32 different persons are rather const. (55.5 to 61.2 dynes per cm.) (pure water 75 dynes per cm.) This surface tension is so low that a further addition of substances with capillary activity does not considerably decrease the surface tension. If an emulsion of phosphatides is added to *human plasma* the surface tension, at once, decreases from 44 dynes per cm. to 36 dynes per cm., but within 45 min. it is again spontaneously increased up to its original value. Repeating the same expt. with *blood* the increase is observed within a still shorter time (4 min.) which proves that the phosphatides combine especially with the red blood cells. The surface tension of the *blood of women* is always considerably higher than *that of men* which explains the greater velocity of pptn. of the red blood cells of women. There is a distinct difference between the *statical* and the *dynamical surface tension of the blood*. Immediately after the formation of a fresh surface 63 to 65 dynes per cm. is observed; this value decreases within 30 to 45 min. to 55 to 60, owing to the action of an unknown colloidal substance. R. BRUTNER

Some new observations on relation of the real sugar content of the urine and the sugar content of the blood. D. G. COHEN-TERVAERT. *Arch. néerland. physiol.* 7, 352-4(1922).—Recent expts. of C.-T. prove that after taking 100 g. of glucose *per os* no increase in the sugar content of the blood takes place in men, although the secretion by the kidneys is increased (cf. Benedict, *C. A.* 12, 1304; and Chabanier, *Arch. urolog.* (Necker) 2, 1(1919)). R. BRUTNER

The permeability of the normal intestinal wall for sucrose. E. SUIJTER. *Arch. néerland. physiol.* 7, 362-5(1922).—Repeating the expts. of Woringer (*C. A.* 16, 3332) S. finds that 0.2 to 0.8% of the sucrose fed to a man appears in the urine. The sucrose is detd. in the urine by measuring the reduction of Fehling soln. before and after inversion. The difference corresponds to the sucrose present. The expts. are repeated with a dog and yielded the same result. The intestinal wall is, therefore, permeable for sucrose to a certain degree. Large differences are found on observing various individuals. R. BRUTNER

The production of carbon dioxide during a lecture. ROBERT TIGERSTEDT. *Arch. néerland. physiol.* 7, 538-42(1922).—Comparing the CO_2 production in perfect rest and while delivering a lecture for 1 hr., an increase of 5 g. is observed (av. of 4 observations). R. BRUTNER

The function of the spleen. HERMANN RAUTMANN. *Deut. med. Wochschr.* 48,

1504-5(1922).—Blood taken from the splenic vein contains fewer erythrocytes than arterial blood. Prolonged ether narcosis augments this difference so that arterial blood may contain one million erythrocytes per cc. more than blood from the splenic vein. Ether narcosis notably lowers the osmotic resistance of the erythrocytes. After an injection of phenylhydrazine, which increases the osmotic resistance of the erythrocytes, the blood from the splenic vein and from an abdominal artery contains identical numbers of erythrocytes. The spleen arrests or destroys only those erythrocytes whose osmotic resistance has been lowered. Animals were injected with typhoid bacilli or wether erythrocytes. Three days after the injection the agglutination titer of the systemic blood (ear vein) was 1:40 while that from the splenic vein was 1:1600. The hemolysis titer was 1:80 for systemic blood and 1:1280 for splenic-vein blood. An injection of adrenaline raised these values markedly for splenic-vein blood; prolonged ether narcosis lowered the values. The spleen appears to play a prominent role in the production of antibodies.

MILTON HANKE

The origin of endocrinology and its present status. E. GLEY. *Rev. gén. sci.* 33, 638-45(1922).—A brief historical survey is given, the half ignored work of Bernard in 1855 being stressed especially. Then follows a discussion of the present status of endocrinology, in which particular attention is called to the complex nature of many glandular secretions, the paucity of definite scientific data regarding their precise functions and the numerous unsolved problems.

T. SWANN HARDING

Presence of the antineuritic and antiscorbutic vitamins in urine. N. VAN DER WALL. *Biochem. J.* 16, 713-26(1922).—Various expts. are recorded to prove the presence of vitamin B and the absence of vitamin C in urine.

BENJAMIN HARROW

The distribution of the combined uric acid in the corpuscles of beef blood. ELIZABETH B. NEWTON AND ALICE R. DAVIS. *J. Biol. Chem.* 54, 601-2(1922).—The combined uric acid compd. in beef blood is contained in the erythrocytes as no uric acid could be detected in the leucocytes or serum, and the figure for total uric acid from the red cells compared closely with that for whole blood. Combined uric acid in human, horse, sheep, pig, dog, and chicken blood. *Ibid* 603-5.—Combined uric acid is present in each of the species of animal studied. The amt. in beef blood far exceeds that in any other animal blood so far analyzed. It was possible to obtain crystals from 600 cc. of human blood but the quantity was too small to weigh. Only traces were found in horse, sheep, pig, dog or chicken blood although 3,500 cc. of sheep blood was used.

A. P. L.

Changes in concentration of the carbon dioxide resulting from changes in the volume of blood flowing through the medulla oblongata. A. B. HASTINGS, HELEN C. COOMBS AND F. H. PIER. *Am. J. Physiol.* 57, 104-9(1921).—When the vol. of blood flowing through the medulla oblongata is reduced by clamping blood vessels there is an increase in magnitude or rate of the respiratory movement, a marked rise of the arterial blood pressure, and a fall in arterial CO_2 . It appears that conditions in the central mechanism itself det. respiratory activity.

J. F. LYMAN

Further experiments on the action of bile on striated muscles. ALESSANDRO ROSSI. *Atti inst. Veneto* 79, 938-47(1920).—R. extended his earlier expts. (cf. *C. A.* 15, 701) showing the stimulating effect of bile on the muscle sarcoplasm. In expts. with frog gastrocnemius muscles he shows that an increased tonus is produced by means of Na glycocholate or by means of decolorized bile. When bile is employed the muscle not only contracts but displays rhythmic oscillatory movements. A study of the simple contraction wave corroborates the view that it is the sarcoplasm which is stimulated by the bile. Depending upon the time during which the muscle is exposed to the action of the bile (5 to 10 min. in 5% bile) the height of the curve becomes smaller than normally, and especially the relaxation phase becomes extended. As the best indication of the loss of elasticity, the curve of contraction in bile does not reveal the descending

curve (below the zero line) on the relaxation side, the curve resembling that obtained with fatigued muscle. S. MORGULIS

Blood of pigeons partially starved on a diet of polished rice. F. MAIGNON. *Compt. rend. soc. biol.* **86**, 1175-6(1922).—As a result of undernutrition on polished rice the blood of pigeons undergoes definite alterations; the number of red cells and the amt. of hemoglobin decrease rapidly and steadily while there is also a tendency towards considerable leucocytosis. S. MORGULIS

The respiratory exchange of inhabitants of high altitudes. J. J. IZQUIERDO. *Compt. rend. soc. biol.* **87**, 639-40(1922).—The measurements were made in Mexico at an altitude of 2240 meters (mean barometer 596 mm. Hg). The av. respiratory capacity was 4 l. per sec. which is considerably greater than that found at lower altitudes. These data are regarded as proof for the view that the max. ventilation is dependent upon the O_2 pressure of the atm. S. MORGULIS

Influence of respiring pure oxygen on arterial blood pressure. LUCIEN DAUTREBANDE. *Compt. rend. soc. biol.* **87**, 793-5(1922).—Respiring O occasions a rise in the CO_2 threshold of the respiratory center owing to a constriction of the capillaries of the medulla. This in turn causes a slowing of the circulation and an increase in H-ion concn. owing to the accumulation of CO_2 , which calls forth a greater ventilation and the alveolar CO_2 tension falls, on the av., about 1.5 mm. Hg. The change in the contraction of the capillaries reveals itself also in the arterial blood pressure, the diastolic pressure being increased and the systolic, on the contrary, diminished. S. MORGULIS

Physico-chemical studies on the mechanism of blood coagulation. The role of ions. I. N. KUGELMASS. *Compt. rend. soc. biol.* **87**, 802-4(1922).—Starting with a plasma-thrombin or a fibrinogen-thrombin system of a p_H less than 7 a diminution in H-ion concn. is observed which resembles an adsorption process, being very rapid at first and approaching an asymptote towards the end of coagulation. The fibrin clot formed has a lower H-ion concn. than that of the original mixt. This change occurs no matter what the initial p_H value of the mixt. The greater the initial H-ion concn. the larger is the difference between the initial and final p_H . On the av. about 50% of the H ions disappear during coagulation. The optimum p_H for coagulation is between 5 and 8. On both the acid and alk. sides of this optimum range, the greater the deviation the less perfectly is the coagulum formed, and the fibrin remains in sepd. shreds. The isoelec. point was detd. for the various blood proteins. This was: for serum-albumin 4.7, serum-globulin 4.55, fibrinogen 8, and for fibrin 7.2 p_H . The optimum coagulation takes place therefore at a p_H about the isoelec. point of fibrin. S. MORGULIS

An experimental study of the genital hormones. J. CORRE. *Compt. rend. soc. biol.* **87**, 842-4(1922).—The following argument underlies C.'s exptl. investigation: If the repression of the development of grafted sexual glands is due to a hormone conflict and if the hormone is colloidal in nature, there should be produced under the influence of the graft antibodies. These antibodies should make a female with a testicular graft anti-male, and the male with an ovarian graft anti-female. The expts. were performed on male and female guinea pigs into which either testes or ovaries were transplanted under the skin. These operated animals were mated with normal animals and they gave birth to both male and female offspring and apparently in normal proportions. This is, therefore, considered to be evidence against the supposition of a sp. antibody production under the influence of the sex gland hormones which would cause either anti-maleness or anti-femaleness in the operated guinea pig. No examn. was made to det. if the male or female characteristics and potency were in any way affected in the offspring. S. MORGULIS

Effects of transfusion of carotid blood collected during splanchnic stimulation.

EDGARD ZUNZ AND PAUL GOVAERTS. *Compt. rend. soc. biol.* 87, 881-2(1922).—Two dogs of approx. the same size were morphinized. In one dog a record of the carotid pressure is taken, while in the other the splanchnic nerve is isolated directly below the diaphragm and stimulated. Canulas are inserted in the jugular veins of both dogs, also in the femoral artery of the first and in the carotid of the second dog. By means of syringes blood from the femoral artery of the first dog (A) is transferred to the second dog (B), while blood from the carotid of (B) is at the same time injected into the jugular of (A). As much as 400 cc. is thus transferred in about 15 min. without any effect being manifested in the carotid blood pressure of dog (A). If, however, 1 mg. of adrenaline is injected into the jugular of dog (B) and then some of its blood transferred to (A) there is a rise in pressure of 4-6 mm. Hg. Even as little as 0.0075 mg. of adrenaline delivered in 120 cc. of blood into dog (B) was sufficient when (B) blood was injected into (A) to produce a marked rise in its carotid pressure. Conclusion: Splanchnic stimulation does not produce enough adrenaline to cause arterial hypertension.

S. MORGULIS

Changes in hydrogen-ion concentration during coagulation of the blood. I. N. KUGELMASS. *Compt. rend. soc. biol.* 87, 883-5(1922).—The cond. of a fibrinogen soln. is diminished while it gels under the influence of thrombin. The clot thus formed must be an irreversible gel owing to the fact that its resistance to the current rises. At the time the clot forms it adsorbs the free ions, as can be shown by washing the clot thoroughly with cold water, filtering and making up the filtrate to the original vol. The H-ion concn. of the latter is always less than that of the initial mixt. Na ions have no effect on the changes in cond. but Ca ions increase and accelerate the changes during coagulation. The formation of the clot is retarded by the presence of Na and still more by that of Ca. Na accelerates and Ca retards the retraction of the clot. It was further noted by a special method of procedure that the Cl ions do not vary before and after coagulation but that the Ca ion like the H ion is partly adsorbed during the process. During the coagulation, when fibrinogen is transformed into fibrin, there is a continuous increase in the protective power of the medium as evidenced by its effect on colloidal gold solns., which indicates an increased colloidal stability of the coagulating mixt., also an increased power of adsorption and of the degree of dispersion. All this attains a max. in the sepg. serum.

S. MORGULIS

Influence of the concentration of different constituents of a thrombin solution on the rapidity of the blood coagulation. I. N. KUGELMASS. *Compt. rend. soc. biol.* 87, 998-9(1922).—The relation between the concn. of the thrombin soln. and the rate of coagulation can be expressed by the empirical equation $C_M = \text{const.}$, where t is the time, k is a const., and C is the thrombin concn. When the different elements comprising the thrombin are analyzed separately (serum, Ca and cytozyme) the above formula loses its exponential character and becomes simply $Ct = \text{const.}$ when either the Ca or the cytozyme do not undergo variation. It follows from these expts. that the serum exercises the principal effect on the coagulation rate, which is thought to depend upon the presence of the serum colloids.

S. MORGULIS

Changes in viscosity and degree of transparency during coagulation. I. N. KUGELMASS. *Compt. rend. soc. biol.* 87, 1000-1(1922).—The viscosity curve during coagulation follows that of an autocatalytic reaction. There is a relatively long latent or pre-coagulation period and a shorter period of the formation of the clot. The duration of the first phase depends upon the thrombin content. This pre-coagulation period may become practically infinite and no clot forms when the thrombin quantity is very small. The low viscosity of the latent period is supposed to depend upon the surface of contact and the period is shorter the greater this surface. During the retraction of the clot the viscosity again diminishes. The same facts indicating the autocatalytic course

of the coagulation reaction can be ascertained by studying the changes in transparency by means of a nephelometer. The loss of transparency, at first very slow, increases rapidly while the clot forms until an equil. is reached. This method, therefore, gives direct demonstration of the agglomeration of the fibrinogen particles which was also considered as the cause of the changes in the viscosity. S. MORGULIS

Influence of coagulation on the amino-nitrogen content of the blood. F. PÉTRIT-
JEAN. *Compt. rend. soc. biol.* **87**, 1001-4(1922).—The blood was obtained from the carotid of dogs, part being placed in paraffined test-tubes and the remainder in unparaffined tubes. The blood samples were deproteinized with $\text{CCl}_3\text{CO}_2\text{H}$ and the filtrate was analyzed for amino N by the Van Slyke method. The results with 20 dogs can be arranged in 3 groups. In the first the blood examd. 8-10 min. and 16-20 min. after bleeding showed a diminution of the amino-N content which, however, increased again when the coagulation was completed. In the second, the amino N continually increased in amt. In the third there was no change during the coagulation process. Expts. with known amts. of amino N added to the blood showed that a certain quantity which varied with the amt. originally added became adsorbed. It is not clear, however, if these changes in recovery are outside the limits of the exptl. error. The adsorption of the amino acid does not reveal any parallelism with the results obtained with coagulating blood. It is thought possible that the amino acids are set free from polypeptide combination by proteolytic enzymes and that depending upon H-ion concn. of the coagulating blood partial deamination results. S. MORGULIS

Summary of publications on insulin to date. Compiled by F. M. ALLEN. *J. Metabolic Research* **2**, 125-40(1922).—A complete bibliography of articles published by Banting, Best and collaborators in 1922 on the pancreatic hormone, insulin. Each reference is accompanied by a detailed abstract of the article. Cf. *C. A.* **16**, 1616, 1980, 2905, 3115, 3116, 3331. W. A. PERLZWEIG

The source of insulin. A study of the effect produced on blood sugar by extracts of the pancreas and principal islets of fishes. J. J. R. MACLEOD. *J. Metabolic Research* **2**, 149-72(1922).—"Potent insulin preps. were readily made from the pancreas of the cartilaginous fishes—the dog fish (*Squalus acanthias*) and the skate (*Raja*). Still more so was this the case with the principal islets of Rennie, which are found in many of the bony fishes, the angler (*Lophius*) and the sculpin (*Myoxocephalus*). Since these are readily available fishes, they may serve as a practical source of insulin. No insulin could be prepd. from the pancreatic tissue proper (zymogenous or acinar) of the representative bony fishes (*Lophius myoxocephalus* and *Zoarces*). Although the anatomical relations of these tissues are still obscure, the above results afford strong direct evidence for the hypothesis that insulin, as its name implies, is derived from the insular and not the zymogenous tissue of the pancreas." W. A. PERLZWEIG

Transmission in series of proteolytic ability initially conferred upon inactive pancreatic juice by enterokinase. C. DELEZENNE AND SUZANNE LEDEBT. *Compt. rend.* **175**, 779-81(1922).—When enterokinase is added to pancreatic juice at 39° the former is consumed or destroyed during the activation of the latter, also the trypsin formed is at the same time deprived of all activating power. The activation is complete in 30 to 40 min. but if the expt. is carried out at 0°, the activation requires 36 to 48 hrs. The degree of activity of the juice was estd. by a detn. of the time necessary for the soln. of 2 cc. of 5% gelatin under given conditions. The liberation of trypsin was considered at a max. when the gelatin was completely liquefied in 15 min. at 39° upon the addn. of 0.002 to 0.003 cc. of the juice. When this degree of activity was attained in the initial juice (I) a mixt. was made of 0.1 cc. of (I) which had been subjected to the action of kinase at 0° for a specified time (48 hrs.) and 0.9 cc. of a new juice (II). This mixt. in 4 hrs. at 0° had the same activity as (I) although only 0.1 as much kinase was present.

A third sample (III) of pancreatic juice was mixed with a portion of activated (II) and held at 0° for several hrs. when it attained the same power to liquefy gelatin as (I) or (II). Juice (III) in like manner activated juice (IV). With rigorous aseptic manipulation and preservation of the juice the activation was effective up to 30 passages.

L. W. RIGGS

Seasonal tide of blood phosphates in infants. A. F. HESS AND M. A. LUNDAGEN. *J. Am. Med. Assoc.* 79, 2210-2(1922).—The seasonal tide of blood phosphates with a diet of raw milk shows a decline from about 4 mg. % in Dec. to 3.5 mg. % in March, after which the blood phosphates quite steadily rose to 4.5 mg. % in June. The low level of phosphates in March would have been lower but for the fact that whenever the phosphates fell to 3.75 mg. % the child was given either sun treatment or irradiation from an artificial source. Ultra-violet light can also raise to normal a subnormal amt. of Ca in the blood. In some expts. 7 mg. % have been raised to 10 by irradiations during 2 or 3 weeks with the carbon arc light. The seasonal variation indicates that the chem. constitution of human blood is not const. for all periods of the year. This probably holds true for other tissues. Marked fluctuations are observed only in young children. Seasonal changes in blood compn. appear to be correlated to certain seasonal diseases.

L. W. RIGGS

The spleen and digestion. II. The spleen and pancreatic secretion. Wm. DEP. INLOW. *Am. J. Med. Sci.* 164, 29-44(1922).—No evidence of a definite trypsinogenic function of the spleen could be obtained.

G. H. S.

Plethysmography of the ventricles. P. WOLFER. *Arch. expll. Path. Pharmacol.* 93, 1-33(1922).—By means of a specially constructed system of levers attached to a recording mechanism the motion and vol. changes of the ventricles of the heart (rabbit) were detd. under normal conditions and under the influence of a no. of reacting substances. It was found, *e. g.*, that the intravenous injection of pilocarpine or pituitrine increased the vol. of both ventricles; that adrenaline reacted upon the left ventricle; that imidazoleethylamine dilated the right heart; that digitalis reacted equally, but slightly, upon both ventricles; and that strophanthine exerts its effect upon the right ventricle. The findings are correlated with the carotid pressure and the mechanism of the reactions is discussed.

G. H. S.

Sedimentation rates of erythrocytes. F. RAUER. *Arch. expll. Path. Pharmacol.* 93, 150-62(1922).—The effect of electrolytes and nonelectrolytes, and of anions and cations, upon erythrocyte sedimentation was detd. Electrolytes exert a definitely inhibitory action upon the sedimentation; nonelectrolytes are almost entirely without effect. In the change caused by electrolytes both anion and cation are involved. *E. g.*, in their effects $Mg > Ba > Ca > Na > K$; and iodide and chloride $>$ nitrate and bromide $>$ acetate $>$ sulfate $>$ citrate. Furthermore, acids vary in their effect, as $HCl > HNO_3 > AcOH$ and citric acid $>$ H_2SO_4 . In general the effect of electrolytes in inhibiting red cell sedimentation parallels the effect exerted upon the swelling of colloidal protein bodies. It thus appears that the effect may be associated with a swelling of the protoplasmic envelope of the erythrocytes.

G. H. S.

Effect of operative procedure on the central nervous system upon the total metabolism and upon protein decomposition. II. H. FREUND AND E. GRAFE. *Arch. expll. Path. Pharmacol.* 93, 285-304(1922); cf. *C. A.* 12, 495.—The spinal cord of dogs was sectioned in either the thoracic region or in the cervical segment. The N elimination per kg. in normal dogs averages 0.27 g.; in those with the cord sectioned in the cervical region it was 0.54 g.; and in those with section of the thoracic cord it was 0.39 g.

G. H. S.

Relation between innervation and the chemistry of striated muscle. I. Creatine content of skeletal muscle in decerebration rigidity and in other forms of hyperinnerva-

tion. J. G. DUSSER DE BARENNE AND D. G. COHEN-TERRAERT. *Arch. ges. Physiol.* (Pflüger's) 195, 370-89(1922).—The creatine content of striated muscle is unchanged by rigidity owing to decerebration or rhythmic stimulation of the spinal cord prepn. When, however, the rhythmic stimulation is superimposed upon the decerebration rigidity a significant increase is found in muscle creatine of some 0.2 to 0.3%. G. H. S.

Physiology of the pineal body. W. KOLMER AND R. LÖWY. *Arch. ges. Physiol.* (Pflüger's) 196, 1-14(1922).—Complete removal of the pineal body in rats in no way modified the growth of the animals nor influenced the processes of reproduction.

G. H. S.

Chemical transfer of nerve stimuli. R. BRINKMAN AND E. VAN DAM. *Arch. ges. Physiol.* (Pflüger's) 196, 66-82(1922).—Two frogs were so adjusted for perfusion that the heart of one animal was connected with the gastric vascular system of the other. Stimulation of the vagus of the first frog resulted in a typical stomach vagus contraction of the second.

G. H. S.

Energy transformation in muscle. VI. Origin of contraction heat. OTTO MEYERHOF. *Arch. ges. Physiol.* (Pflüger's) 195, 22-74(1922); cf. *C. A.* 16, 2545.—When muscle is subjected to elec. fatigue under anaerobic conditions of contraction the calorific quotient of lactic acid at 14 and 22° averages 370 cal. When the lactic acid formation and heat production are detd. with minced muscle in phosphate soln. the calorific quotient is almost exactly 200 cal. The reaction heat of lactic acid with the substance of intact muscle is wholly, or almost entirely, referable to the concn. of H ions, and the difference in the heat values found is undoubtedly associated with the disoc. of proteins, since while in the neutralization of 1 g. of lactic acid by phosphate or carbonate some 20 cal. are produced this figure is considerably increased if protein-contg. fluids, as blood serum, egg albumin, yeast ext., or casein, are present. The temp. coeff. of lactic acid formation in minced muscle is between 2 and 3; in intact muscle it is about 4. G. H. S.

Comparative concentrations of alcohol in human blood and urine at intervals after ingestion. W. R. MILES. *J. Pharmacol.* 20, 265-319(1922); cf. *C. A.* 16, 2922.—The EtOH concn. in venous blood and in urine after taking 27.5 g. abs. EtOH dild. in 1000 or 100 cc. of fluid is not identical and does not run parallel in the 1st 2 hrs. after ingestion. Taken as 2.75%, the concns. in the venous blood at 20, 40, 70, and 120 min. after ingestion are 18, 24, 30 and 30 mg. EtOH per 100 cc., while the corresponding urine values are 15, 37, 47 and 43 mg. The urine concn. is 40-50% higher than the blood at 40 min. to 2 hrs. after ingestion and it is also higher than that of the plasma by 20-25%. The EtOH taken as 27.5% gave at the above specified intervals 28, 42, 43 and 36 mg. per 100 cc. in the blood, and in the urine 24, 51, 65, and 49 mg. The same wt. of EtOH taken in a concd. soln. produces a definitely higher EtOH concn. in both blood and urine than when taken in a much more dil. soln. During the 1st 20-30 min. after ingestion the urine EtOH is about the same or a little higher than in the blood; then for 1 hr. or more it is 35-50% higher. The plasma contains a higher EtOH content than the corpuscles in the ratio of about 2:1; but the urine is usually higher than the plasma. Subjects thoroughly habituated to alc. absorb the 2.75% dose about the same as non-habituated individuals. Changes in the amt. of urine per min. do not perceptibly influence the concn. of EtOH in the urine. The % of EtOH eliminated in the urine within 2 hrs. after ingestion is 1.2 to 1.6 of that ingested. The major part of the elimination occurs in this period provided the bladder is emptied 2-3 times. Both blood and urine reach their max. EtOH concn. at about the same time and while not identical still the urine-EtOH curve is useful for comparison with the time relations of the objective measurements of the EtOH effects on the central nervous system. Bibliography of 82 titles.

C. J. WESS

G—PATHOLOGY

H. GIDEON WELLS

Demonstration of food proteins in human breast milk by anaphylactic experiments on guinea pigs. Their probable relationship to certain diseases of the nursing infant. A preliminary report. W. R. SHANNON. *Am. J. Diseases Children* 22, 223-31 (1921).—By injection of milk of mothers receiving eggs as a part of their diet into egg sensitized guinea pigs, intrathecally, an anaphylactic reaction was obtained, indicating the transition of egg proteins into mothers' milk.

S. AMBERG

Ultra-violet radiation in rickets. Effect on the calcium and inorganic phosphorus concentration of the serum. B. KRAMER, H. CASPARIS AND J. HOWLAND. *Am. J. Diseases Children* 24, 20-6(1922).—Before treatment of rickets with a Hg-vapor quartz lamp the inorg. P of the serum was from 2.7 to 3.2 mg. Under treatment, it gradually increased to a max. of 6 mg.

S. AMBERG

The significance of the hemagglutination groups for free transplantation and the change of the agglutination group by medicines, narcosis and Röntgen raying. R. EMM. *Deut. med. Wochschr.* 48, 85-7(1922).—Quinine, Ca lactate, antipyrine, liquor potassium arsenicosum, CHCl_3 , ether narcosis and X-ray treatment changed the blood grouping of patients for various periods of time.

S. AMBERG

The chemical composition of the flocculent precipitate formed in the serological lues reaction. E. EPSTEIN AND F. PAUL. *Deut. med. Wochschr.* 48, 89-91(1922).—Klosterman and Weisbach did not bring sufficient proof of the presence of protein in the flocculent ppt. of the Sachs-Georgi reaction.

S. AMBERG

Cholesterol content of Kupfer cells. Histochemical reaction. A. STOCKER. *Deut. med. Wochschr.* 48, 93-4(1922).—The reaction of Golodetz can be used for the demonstration of cholesterol. A mixt. of 5 parts concd. H_2SO_4 and 3 parts 30% CH_2O colors free cholesterol brown; cholesterol esters are not stained. In the liver tissue of a case of paralysis, free cholesterol could be demonstrated in frozen sections. They are placed in weak formalin soln. and before use transferred to 30% formalin for 5-10 min. The section placed on the slide is treated with a drop of concd. H_2SO_4 .

S. AMBERG

A new turbidity reaction for syphilis. C. F. MEINICKE. *Deut. med. Wochschr.* 48, 384-5(1922).—Balsam of Tolu in alc. soln. is added to the cholesterolized lipid ext. The result depends on whether the tubes are transparent or not. They are read after 1 hr. in the incubator and again after 2 hrs. more, when the weaker reactions become more pronounced.

S. AMBERG

The constant occurrence of bilirubin crystals (hematoidin crystals) in the urine of cases of icterus and their erroneous designation as tyrosine needles. J. DORNFR. *Deut. med. Wochschr.* 48, 453-4(1922).—In nearly every case of icterus with an acid urine contg. leucocytes a condensation of bile pigment could be found in the leucocytes. In some leucocytes needles of crystals can be seen and bundles of needles whose points protruded outside the cells. On addition of HNO_3 with a trace of fuming acid to the centrifuged sediment the needles did not take on a green color, while the bile pigment did. Lugol soln. did not stain the needles green. The diazo reagent used according to Van den Bergh did not give a bilirubin reaction, which is explained by the fact that the substance is not in soln. NaOH hardly dissolves the needles, neither does HCl. Tyrosine reactions were negative. The crystals are considered as hematoidin crystals. Tyrosine and leucine are not found in urine as frequently as has been stated. Yellowish discolored NH_4 urate has been mistaken for leucine.

S. AMBERG

Preservation of forensic sera and antisera with yatrien. G. STRASSMANN. *Deut. med. Wochschr.* 48, 487-8(1922).

S. AMBERG

The "lipoid-splitting" function of lymphocytes. L. ASCHOFF AND H. KAMIYA.

Deut. med. Wochschr. **48**, 794-6(1922).—With Metschnikoff and Ehrlich and against Bergel, no evidence could be seen that lymphocytes split lipoids. S. AMBERG

The possibilities of further simplification of my turbidity reaction. H. DOLD. *Deut. med. Wochschr.* **48**, 797-8(1922); cf. *C. A.* **16**, 1981.—The reaction should not be read before a lapse of 4 hrs. at 37°. Smaller amts. of fluid may be used but this is not advisable. S. AMBERG

The phosphorus content of blood, particularly in carcinoma patients. JOH. VORSCHÜTZ AND JOS. VORSCHÜTZ. *Deut. med. Wochschr.* **48**, 861-3(1922).—The P of 10 cc. defibrinated blood is oxidized by the moist method of Neumann and the total P detd. as P_2O_5 . In 4 normal individuals the P_2O_5 of 10 cc. defibrinated blood was 11.0-11.8 mg. In various patients it varied from 7.8 to 23.8. This P figure divided by the number of red blood cells in millions gives the P quotient, which was normally 2.6-2.9. In a number of carcinoma patients this quotient became higher, about 3.3-4.0, as well as in some febrile conditions. In some cases, the P of the red blood cells was detd. separately. In two normal cases, the serum P_2O_5 was 4.5 and 5.5 mg., that of the red blood cells 15.5 and 12.0 mg., while in two cases of cancer the red blood cells had 20.3 and 17.8 mg. P_2O_5 . Much stress is laid on values over 15 mg. S. AMBERG

The serodiagnosis of syphilis by flocculent precipitate. BRECK. *Deut. med. Wochschr.* **48**, 825-6(1922).—An alc. heart ext. is prepd. which keeps for several weeks. It must be well shaken before the test. Of inactivated serum 0.2 cc. is placed in a test-tube and 0.8 cc. 10% NaCl is added, then 0.2 cc. of the ext. The mixt. is shaken and centrifugalized 20 min. Then the fluid is water clear, with a whitish skin on the surface. On lightly shaking this skin dissolves itself again into a diffuse turbidity without flocs; reaction is negative. If it forms flocs the reaction is positive. The reaction can even be carried out with active serum or even with fresh whole blood, but is less striking. S. AMBERG

The determination of the sedimentation velocity of red blood corpuscles as diagnostic aide. E. ABDERHALDEN. *Münch. med. Wochschr.* **68**, 973(1921).—It is recommended to test the sedimentation velocity of red blood corpuscles not only in their own plasma but also in other plasma, and to test the agglutinating action of plasma on blood of other provenience. S. AMBERG

Calciuria. K. M. HASSELMANN. *Münch. med. Wochschr.* **68**, 1080(1921).—There was no indication that the excretion of Ca in the urine in calciuria is due to an impoverishment of the organism in alkali. S. AMBERG

Alimentary urobilinogenuria (bile test). W. FALTA, F. HÖGLER AND A. KNOBLOCH. *Münch. med. Wochschr.* **68**, 1250-1(1921).—Dry ox bile in doses of about 3 g. in wafers is well tolerated. Normal individuals or patients with no indication of liver injury did not show urobilinogen in the urine; patients with liver injury did. S. A.

Constant changes in the amounts of blood lipoids after injections of substances foreign to the body as is done with the so-called stimulation therapy. E. GABBE. *Münch. med. Wochschr.* **68**, 1377-9(1921).—The blood serum was tested by stratifying 0.5 cc. with 0.5 cc. 5% glycerol for ring formation after 24 hrs. in the incubator at 37°. The lipid detns. were made with Bang's micro-method, modified because proper petrol. ether could not be had. Therefore the alc.-sol. fatty substances had to be taken. (Reduction of a chromate soln. by saponified lipoids after evapn. of alc. in H_2SO_4 soln., titration of the excess chromate with 0.1 N thiosulfate.) Cholesterol was detd. by the Autenrieth and Funk method. The lipid detns. are not free from objections and should be re-tested by a better method. In the paper the values are given in terms of fatty acid. Injections of collargol, milk, caseosan, hypertonic NaCl, glucose, cane sugar, argochrome and horse-serum in man are constantly followed by variations in the lipid content of the blood, cholesterol as well as very probably the phosphatides. Small

doses, giving little or no rise of temp., lead to an increase lasting several hrs., larger doses followed by high fever to a transitory decrease which is followed in the majority of cases by an increase above the original amt. The intensity of the serum ring test with 5% glycerol seems to indicate rather well the variations in the blood lipoids. S. AMBERG

The demonstration and the behavior of extract lipoids in the different precipitation reactions. P. NIEDERHOFF. *Munch med. Wochschr.* 68, 1419-20(1921).—Discussion of methods by which the material for analysis has been obtained. S. A.

Artificial virulence and chemistry. BACHMANN. *Munch med. Wochschr.* 68, 1589-90(1921).—Much reported that he was able to render harmless saprophytes virulent for mice and guinea pigs on simultaneous injections of lactic acid. B. could not confirm these results. S. AMBERG

Vitamin starvation, immunity and virulence. C. SETTI. *Biochim. terap. sper.* 9, 197-206(1922).—Pigeons fed on polished rice show less resistance to attenuated infections than do normal birds, and the latter develop more powerful immunity where vaccines are employed. Feeding expts. are tabulated so as to show the relation that immunity and virulence of infections bear to the vitamin content of the diet.

H. W. BANKS, 3RD.

The proof of complement fixation in human tuberculosis. S. RAPISARDI. *Biochim. terap. sper.* 9, 229-44(1922).—With a few exceptions the reaction is specific, and of value in prognosis. A large bibliography is given. H. W. BANKS, 3RD.

The use of calcium in pulmonary tuberculosis. T. J. BEASLY. *Am. Rev. Tuberculosis* 6, 407-9(1922).—During the past 12 years B. has observed that the clotting time of the blood of many tuberculous patients is prolonged in ratio to the time the disease has existed and the extensiveness with which it has progressed. Patients, who showed a prolonged coagulation time, and to whom Ca has been administered, invariably show in due time a return to the normal, or even less than the normal coagulation time. The use of CaCl_2 intravenously is preferred, but a drawback exists in that certain patients react violently to the injections. Finally use is made of a mixt. of 5 g. of anhyd. CaCl_2 with 60 minims of cod-liver oil and 1 g. of Fe, given after each meal.

H. J. CORPER

Studies in the chemotherapy of bacterial infections. III. Experimental tuberculous pleuritis as an aid to chemotherapeutic investigations in tuberculosis. J. A. KOLMER and ISANU OGAWA. *Am. Rev. Tuberculosis* 6, 437-53(1922); cf. *C. A.* 16, 4282.—The method of producing exptl. tuberculous pleuritis in guinea pigs, rabbits, dogs and white mice is described for use in chemotherapeutic studies in tuberculosis.

H. J. CORPER

Permanent pulmonary effects of gas in warfare. J. L. HAWKINS and W. C. KLOTZ. *Am. Rev. Tuberculosis* 6, 571-4(1922).—The cases disclosed a definite and clinical picture of chronic bronchitis, varying in its degree of severity, with or without accompanying emphysema. This form of bronchitis produces a certain degree of functional disability. A majority of the cases were diagnosed as clinical tuberculosis but no attempts were made to show any connection between the effects of the gas and the coexisting tuberculosis. Only 25% of the cases gave a history of influenza or pneumonia.

H. J. CORPER

The serum ring reaction in tuberculosis. M. A. SMERTON. *Am. Rev. Tuberculosis* 6, 588-90(1922).—The test employed by Krumwiede and Valentine (Parke & Williams: *Pathog. Microg.* pp. 318) for the rapid defn. of pneumococcus types was used as follows: the sol. antigen from sputum was floated on top of serum; but in no case was a reaction observed. O. T. was then used in place of the sputum antigen ext. with very definite results. The presence or absence of natural complement appears to play no part in the reaction, since the ring formation was noted in both fresh and inactivated

sera. 150 human sera were tested and while the reaction is well defined and apparently occurs with greater frequency in tuberculous persons than in normal ones, it is not sp. The test does not indicate the degree of immunity possessed by the individual and consequently is of no prognostic value.

H. J. CORPER

The biochemistry and chemotherapy of tuberculosis. XXIII. The chemical composition of calcified tuberculous lesions. MARY E. MAVER AND H. G. WELLS. *Am. Rev. Tuberculosis* 6, 649-58(1922).—Calcified peribronchial lymph nodes and pulmonary lesions contain a small proportion of SiO_2 , but not more than uncalcified peribronchial lymph nodes or lung tissues contain in adults. This SiO_2 is derived chiefly, if not entirely, from inhaled siliceous dust, for calcified tuberculous mesenteric lymph nodes do not contain appreciable amts. of SiO_2 , and only a trace was found in a calcified tuberculous pleural exudate. Therefore, these analyses furnish no chem. evidence supporting the hypothesis that SiO_2 plays an important part in the healing of tuberculous lesions. Calcified tuberculous lesions resemble in compn. other calcified pathol. tissues and also normal bone.

H. J. CORPER

A clinical study of 289 serum reactions with tuberculo-antigens. P. M. ANDRUS. *Am. Rev. Tuberculosis* 6, 694-701(1922).—This serological study consisted of complement-fixation tests with tuberculo-antigens (Petroff's glycerol ext.), the inhibitive reaction of Caulfield (*J. Med. Res.* 26, 101(1911); cf. *C. A.* 7, 1224) and Wassermann tests. Cross or fake fixations between Wassermann-fast and tubercle-fast antibodies are not the rule, but can nevertheless be demonstrated in individual cases. The presence of these reactions *per se* cannot establish a diagnosis other than that of biol. tuberculosis; the stronger and more persistent the reactions, however, the greater are the probabilities that the patient is fighting a clinical or subclinical tuberculous lesion. The tests have by far the greatest value in prognosis and as a guide to treatment in the individual case.

H. J. CORPER

A new treatment in tuberculosis. F. JESSÉN. *Z. Tuberk.* 37, 33-7(1922).—The waxy capsule of the tubercle bacillus is one of its greatest protections against chemotherapeutic agents introduced into the body. The caseation tissue which harbors the bacilli and is devoid of blood circulation is another protective factor. The rational therapy of tuberculosis should attempt to build up a defensive mechanism against the tubercle bacillus in the body itself. For this purpose a protective mechanism is stimulated according to Abderhalden's conception of "defensive ferments" by means of an ether ext. of tubercle bacilli which is injected into normal animals; when a necrotic papule with inflammatory reaction at the site of the injection results, blood is withdrawn from the animal and is diluted. The prepn. thus obtained is called the "ether-extract antibodies." The prepn. is used as an inunction in cases of pulmonary and glandular tuberculosis, it is said, with good results. The same method can be used in differentiating between tuberculous and non tuberculous glandular enlargements. An ether ext. of a microorganism (not a tubercle bacillus) found in an enlarged gland of a child was thus prepd., and the child treated by inunction with this prepn. recovered. In incipient pulmonary cases invariable success attained, while cases of laryngeal and far advanced pulmonary tuberculosis were favorably benefited.

H. J. CORPER

The specific gravity of the urine. T. ADDIS AND MARJORIE G. FOSTER. *Arch. Intern. Med.* 30, 555-8(1922).—Urea does not increase the sp. gr. of a soln. as much as NaCl and NaH_2PO_4 do in the same concn. The same difference in the sp. gr. of the urine was observed after the ingestion of identical quantities of these substances. "It is therefore concluded that sp. gr. detns. cannot form part of any method intended to measure the amt. of secreting tissue in the kidney." A test of the capacity of the kidney to produce a urine of high specific gravity. T. ADDIS AND MARLAN C. SHEVSKY. *Ibid* 559-62.—An attempt was made to fix conditions so that a detn. of the sp. gr. of

the urine might be of diagnostic value. The subject is instructed to partake of his usual diet but not to drink any fluids, including milk, for 36 hrs., beginning in the evening. The urine of the last 12 hrs. (night) is collected. In 94 specimens collected from 75 normal individuals, the sp. gr. varied from 1026 to 1039, av. 1032. The values were not appreciably affected by the ingestion of a lb. or more of steak with the last meal. Slightly lower values, 1020-1033, av. 1027, were obtained with 6 subjects who had been on low-salt low-N diet for 48 hrs. before the collection of the urine. The diagnostic value of a low sp. gr. may be doubtful but that of a high sp. gr. is unmistakable.

I. GREENWALD

Studies on blood lipids. I. The relation of cholesterol and protein deficiency to basal metabolism. A. A. EPSTEIN AND HERMAN LANDE. *Arch. Intern. Med.* 30, 563-77(1922).—A low blood cholesterol was found associated with high basal metabolism and a high blood cholesterol with a low basal metabolism. Thus, a low blood cholesterol was observed in hyperthyroidism and a low basal metabolism in nephrosis. I. G.

The alkali reserve in "Röntgen-ray" sickness. ROSS GOLDEN. *Arch. Intern. Med.* 30, 629-37(1922).—"No evidence that the constitutional reaction following irradiation with Röntgen rays is associated with a lowered alkali reserve was found in several detns. of the plasma CO_2 -combining power of 4 patients and in repeated detns. of the plasma CO_2 content of 3 dogs."

I. GREENWALD

Osteomalacia. E. P. CORSON WHITE. *Arch. Intern. Med.* 30, 620-8(1922).—Osteomalacia occurs in several families of mammals and of birds and, in the Philadelphia Zoölogical Gardens, was particularly common among Cebidae monkeys. Their food was subjected to chem. and biol. analysis. It was found to be poor in protein, which was also of poor quality, and poor in fat. The ash content was low and, although acid, was poor in P. The diets were deficient in vitamins A, B, and C, being particularly poor in A.

I. GREENWALD

Cholera acidosis and its therapy. M. TSURUMI AND T. TOYODA. *Arch. Intern. Med.* 30, 796-800(1922).—The number of drops delivered from a stalagmometer by a mixt. of blood plasma and a soln. of quinine-HCl in unit time was used as a measure of the alkali of the blood. The greater this is, the greater is the amt. of quinine liberated and the greater is the number of drops. The plasmas of 5 normal men and 5 normal women gave readings of from 67.5 to 68.6, av. 68 drops. The cholera patients were examd. upon admission to the hospital. The mild cases (19) gave an av. of 67.9 drops; the moderately severe cases (11, including 1 that died) gave an av. of 67.7 drops; the severe cases (19, of which 13 were fatal) gave an av. of 66 drops. Injections of NaHCO_3 generally increased, but sometimes decreased, the number of drops, perhaps because the acidotic process was sometimes too severe to be overcome by the injection. The mortality in a group of 49 cases treated with NaHCO_3 -NaCl injections was 28.4%; in a group of 480, treated with injections of NaCl soln. or serum, or both, the mortality was 42.7%.

I. GREENWALD

The anemia of chronic nephritis. GEO. F. BROWN AND GRACE M. ROTH. *Arch. Intern. Med.* 30, 817-40(1922).—Of 187 cases of chronic glomerular nephritis, the blood of 105 had a hemoglobin content of less than 70% (Dare) and an erythrocyte count of less than 4,000,000. The amt. of blood in the urine and feces was altogether too small to account for the anemia. Neither could this be accounted for by the amt. of hemolytic substances in the urine as compared with the amt. in the urine of non-anemic persons, nor by a reduced protective action of the serum as measured against hypotonic NaCl solns. Detns. of urobilin and urobilinogen in the duodenal contents did not indicate an increased blood destruction. The morphological picture, the rate of development, the lack of response to transfusion, or administration of Fe or As, indicate a failure in blood formation. This is not due to loss of albumin in the urine for no such anemia

was observed in cases of orthostatic albuminuria, nephrosis, focal nephritis or chronic passive congestion, nor to the low protein diet, for no anemia was observed in cases of hypertension without apparent renal involvement on similar diets; nor to hydremia, for there was no increase in blood volume and the decrease in concn. of the plasma, as measured by the albumin, was slight (about 2%), nor could the anemia be related to the previous retention of urea, creatinine or uric acid. The *basal metabolism* in the 10 patients examd. was from -15 to +15% of the normal, except in 1 case in which it was +18%. It is believed that the defective blood formation and the nephritis are due to the same cause.

I. GREENWALD

The relation between ingested fat and the lipemia of diabetes mellitus. P. L. MARSH AND H. G. WALLER. *Arch. Intern. Med.* **31**, 63-75(1923).—Diabetic patients were placed on a low-calorie diet, which, after the urine had become sugar-free, was gradually increased to cover the requirements of the patient. It contained as much as 4 g. fat per kg. body-wt. per day. There was no hyperlipoidemia, not even in 4 patients who, on admission, had shown a fat content, in the blood, of from 2 to 4%. Cf. Blath-erwick, *C. A.* **16**, 749.

I. GREENWALD

Defects in the membranous bones, diabetes insipidus and exophthalmus, with report of a case. L. C. GROSH AND J. F. STIFEL. *Arch. Intern. Med.* **31**, 76-84(1923).—Report of a case of diabetes insipidus, exhibiting defects in the membranous bones of the skull and pelvis, exophthalmus and some degree of dwarfism. Subcutaneous injections of *pilulari* ext. at first temporarily controlled the polyuria but later were ineffective.

I. GREENWALD

Hippuric acid synthesis as a test of renal function. SERGIUS MORGULIS, G. P. PRATT AND H. M. JAHR. *Arch. Intern. Med.* **31**, 116-44(1923).—In normal persons, 2 g. of BzOH, administered as such or as the Na salt, is completely synthesized to hippuric acid and the kidney is stimulated to enhanced activity. In nephritic and cardiorenal patients the synthesis is never complete but, even in severe nephritis, from 53 to 95% of the ingested BzOH may be recovered as hippuric acid and from 59 to 100% as total BzOH in the 24 hrs. following the administration of BzOH. [A few figures are reported for the 6-hr. excretion but none for the 3-hr. period which was proposed by Kingsbury and Swanson (*C. A.* **15**, 3673) ABSTR.]

I. GREENWALD

The behavior of chlorides introduced into the blood under normal and nephritic conditions. F. P. UNDERHILL AND E. T. WAKEMAN. *J. Biol. Chem.* **54**, 701-15(1922).—Two rabbits, weighing 2-3 kg., were bled from the ear, about 2 cc. being taken each time, at intervals at first of a few min., then of hrs. It was found that the hemoglobin (Hb) content of the blood might diminish, with a consequent increase in Cl content. Two other rabbits were similarly bled after the intravenous injection of 80 cc. 0.9% NaCl in 2 min. Both injected NaCl and fluid largely disappeared from the circulation within 5 min. and the Cl content of the blood returned to normal within 30 min. In 2 animals that had received, subcutaneously, 1 g. tartaric acid neutralized with NaOH, on the preceding day, the same rapid disappearance of NaCl and fluid from the circulation was observed but the return to the normal Cl content of the blood appeared to be delayed. This U. and W. ascribe to some altered permeability of the capillaries of the general circulation. [Perhaps it was due to the failure of secretion of urine in these animals. ABSTR.] In 1 nephritic rabbit, the concn. of Hb and of NaCl in the blood was followed for several days. As the secretion of urine was resumed, the NaCl of the blood returned to its normal value, although the Hb concn. remained low. I. G.

The oral administration of antigens and its relation to anaphylaxis. Studies with guinea pigs, egg albumin and horse serum. SHIN MAIE. *Biochem. Z.* **132**, 311-24 (1922).—When egg albumin and horse serum are given by mouth to guinea pigs there usually follows a sensitizing of the organism of such a nature that subsequent intravenous

reinjection of the particular antigen produces death in anaphylactic shock. The reaction is obtained with young as well as with older animals from which it can be presumed that the intestinal wall is permeable to the proteins used in both cases. As a rule the transference of antigen into the peripheral blood after oral administration can be tested in young animals by the complement fixation and precipitin tests. Older animals alone give negative reactions, which may be due to the larger surface and consequent diln. When egg albumin is given *per rectum* a sensitization can be demonstrated. Horse serum similarly administered gives no anaphylactic test. Neither antigen can be detected by the complement fixation or the precipitin reaction when given *per rectum*. It may be that the lower bowel is less permeable to the antigens. When the 2 proteins are given either by mouth or intravenously and then by mouth no anaphylactic symptoms are obtained.

F. S. HAMMETT

Physico-chemical studies of carcinoma. N. WATERMAN. *Biochem. Z.* 133, 535-97(1922).—The Ca concn. of the blood is dependent on the actual and potential reaction. The titration of 49 plasmas from tumor patients showed a mean increase of 10% in alky. The p_H was also higher than normal. The results were confirmed that the increased alky. is due to org. as well as inorg. constituents. The detn. of alky. in urine is not of value in this problem. A large % of urines from tumor-bearing patients show a lessened degree of acidity and NH_3 excretion. An ingenious app. for studying permeability in tissues and a discussion of its applicability are given, together with microchem. studies of tissues. The paper is too extensive for brief abstraction.

F. S. HAMMETT

Chemical studies of the blood in tuberculous rabbits during the tuberculin reaction. C. MEYERSTEIN. *Biochem. Z.* 134, 139-45(1922).—Of 6 rabbits, 5 gave a positive tuberculin reaction, 2 of these after the 2nd injection. The chem. and phys. studies of the blood of these animals during the course of the reaction showed that no changes occurred in the blood sugar, NaCl or serum concn. as detd. by the refractometer.

F. S. HAMMETT

The Bruck flocculation reaction for the serodiagnosis of syphilis. JOHANNES ZEISLER. *Deut. med. Wochschr.* 48, 1510-11(1922).—A comparison of the method of Bruck with that of Wassermann for the serodiagnosis of syphilis showed that identical results were obtained when either reaction was distinctly positive or negative (93.4% of the 1031 cases reported). In cases giving a doubtful, weakly positive or weakly negative Wassermann reaction, divergent results were obtained with the method of Bruck. This occurred in 51 of the 1031 cases investigated. Results that were entirely contradictory were obtained in only 0.8% of the sera investigated. The method of Bruck can be recommended as a substitute for, or as an adjunct to, that of Wassermann because of its equal reliability and its greater simplicity.

MILTON HANKE

The ingredients of organ extracts that are active in the serological diagnosis of syphilis. EMIL EPSTEIN AND FRITZ PAUL. *Deut. med. Wochschr.* 48, 1648-9(1922).—A criticism of the article bearing the same title published by Klostermann and Weisbach (*C. A.* 16, 3961).

MILTON HANKE

Leucine and tyrosine in urine in icterus. F. GOEBEL. *Klin. Wochschr.* 1, 1158 (1922).—Gérone (*C. A.* 17, 140) found crystals of tyrosine and leucine in the urine of icteric patients. Most of his detns. consisted in crystallographic studies of concretions isolated from such urines. Crystals that look like leucine and tyrosine may be obtained in such cases, but they are neither tyrosine nor leucine. This was shown by means of the β -naphthalenesulfonyl chloride, the β -naphthyl isocyanate and the phenyl isocyanate methods.

MILTON HANKE

A method for the demonstration in serum of enzymes that are foreign to normal blood. (A contribution to the diagnosis of organic diseases.) P. RONA, H. PETOW

AND H. SCHREIBER. *Klin. Wochschr.* 1, 2366-7(1922).—Although quinine completely inhibits the normal lipase of human serum, it does not inhibit the liver lipase. In hepatopathics, the serum contains not only the normal serum lipase but some liver lipase as well. If quinine is added to such serum, the lipolytic action is reduced, because of the inhibition of the serum lipase, but it is not completely destroyed. The following method was used: 3 cc. of serum are mixed with 3 cc. of a PO_4 buffer mixt. (1 part 0.33 M NaH_2PO_4 and 14 parts 0.33 M Na_2HPO_4 , p_H 7.6) and 1 cc. of a 0.2% quinine-HCl soln. A control is prepd. as above with 1 cc. of H_2O in place of the quinine. The solns. are allowed to stand for 0.5 hr. At the end of this time the liquid is mixed with a clear, satd. soln. of tributyrin. Immediately after the mixing and at time intervals of 3, 30, and 60 minutes, some of the liquid is subjected to a stalagmometric detn. according to Rona and Michaelis. Hydrolysis of the tributyrin leads to an increase in the surface tension of the liquid and a decrease in the no. of drops per cc. In subjects with normal livers the quinine treatment completely inhibits the lipolytic action of the serum; the surface tension of the serum tributyrin soln. is unchanged after one hr. The surface tension of the quinine-treated serum, tributyrin soln., in the case of hepatopathics, steadily increase (indicating hydrolysis of the tributyrin), the no. of drops per cc. steadily decrease. The serum of a no. of nephritics also contained quinine stable lipase, probably kidney lipase.

MILTON HANKS

Reactive hypoglycemia after the parenteral administration of sugar. RUBINO AND VARELA. *Klin. Wochschr.* 1, 2370-4(1922).—When glucose is introduced into the rectum, drop by drop, sugar appears in the urine; but the blood sugar value is reduced. Hypoglycemia occurs even when a dil. glucose soln. is administered very slowly. Since most of the rectal blood supply empties directly into the inferior vena cava without passing through the liver, these results would suggest a difference in the effect upon the body cells of the commercial glucose and that liberated from glycogen by the liver. The occurrence of a hypoglycemia with glucosuria after the per oral ingestion of glucose by hepatopathics would indicate that in such cases the liver cells are unable to convert the glucose into glycogen and back into systemic glucose in the normal way. Body glucose apparently differs, perhaps stereochemically, from ordinary glucose. M. H.

Use of pancreatic extract in diabetes. C. S. SHERRINGTON. *Nature* 110, 774 (1922).—An address.

BENJAMIN HARROW

Non-specific desensitization. C. H. KELLAWAY AND S. J. COWELL. *Brit. J. Exptl. Pathol.* 3, 268-82(1922).—The intravenous injection of normal guinea-pig serum into actively sensitive guinea pigs causes a degree of protection against the specific antigen which is of only short duration. This loss and subsequent return of the sensitiveness of the anaphylactic animal are explained by parallel changes in the sensitiveness of the plain muscle. The changes in the sensitiveness of the plain muscle are probably due to physical changes occurring in the muscle cells. The demonstrable antibody of the serum is greatly diminished in amt. very soon after the injection of serum, and is not restored till long after the sensitiveness of the plain muscle has returned to its original value. The injection of guinea-pig serum into guinea pigs with a high titer of circulating antibody is followed by the appearance of enhanced sensitiveness of the whole animal during two periods—one shortly after the injection, and a second after the restoration of the sensitiveness of the plain muscle but before the return to normal of the demonstrable circulating antibody.

HARRIET F. HOLMES

The occurrence of a toxic substance in the blood in cases of bronchial asthma, urticaria, epilepsy and migraine. W. STORM VAN LEEUWEN AND ZRYDNER. *Brit. J. Exptl. Pathol.* 3, 282-6(1922).—Blood drawn from a vein was at once mixed with alc., the alc. ext. evapd. and the residue taken up with saline soln. The effect of the ext. on loops of isolated cat intestine was tested. Normal blood exts. had no effect, but

exts. from blood of patients suffering from asthma, urticaria, migraine and epilepsy caused contraction comparable with that produced by pilocarpine (equal to 1-5 mg. pilocarpine per l. of blood). This toxic substance may be related to the allergic disposition.

HARRIET F. HOLMES

Application of the absorption-of-agglutinin test to the serological study of pneumococci. E. R. ARMSTRONG. *Brit. J. Exptl. Pathol.* 3, 287-95(1922).—Agglutination by specific pneumococcal serums is not invariably sufficient for recognition of type. The absorption-of-agglutinin test affords satisfactory confirmation. The use of the absorption test has led to the identification of sub-types of Type I and Type III pneumococcus comparable to the sub-types 2A and 2B of Type II already differentiated by Avery. Sub-type strains exhibit limited specificity within the group to which they belong; in no case has a serum prepd. against a sub-type pneumococcus agglutinated the standard type strain. The serum of rabbits inoculated with the standard Type II pneumococcus is particularly rich in subordinate agglutinins. This property is shared by sub-type 2 strains in general, since the sub-type serums were found to agglutinate pneumococcus strains which had failed to react with any of the 3 standard serums. By this means a degree of serological relationship between the Type II group and salivary streptococci of the *S. viridans* group has been demonstrated. Salivary streptococci are sharply differentiated from pneumococci by their vigorous agglutino-genic properties.

HARRIET F. HOLMES

Iron incrustation of the connective tissue substance in hemochromatosis and in focal hemorrhages. HEINRICH SCHUPPISER. *Arch. path. Anat.* (Virchow's) 239, 320-49(1922).—Observation was made in a case of generalized hemochromatosis of selective incrustation of the reticulum fibers of the retroperitoneal lymph nodes with iron, and a further deposition of lime salts on the iron-incrusted fibers, and in two cases of *struma nodosa* and in the spleen in a case of *lymphogranulomatosis* of a deposition of iron hydroxide and iron phosphate in the form of concretions in a collagenic substrate.

E. R. LONG

The etiology of gall stones. S. F. OLIVER. *J. Lab. Clin. Med.* 8, 242-50(1923).—Bile obtained at operation from gall stone cases and normal bile were allowed to stand in sealed test-tubes, following chem. examn. for bile salt content. All specimens deficient in bile salts deposited cholesterol in the bottom of the tube within a period varying from 3 days to 3 weeks. Normal bile or bile rich in bile salts remained free from such deposit. In a number of tubes cholesterol settled out in concentric layers alternating with pigment, the product bearing a striking similarity to true gall stones. The formation of gall stones *in vivo* is explained as follows: bile stasis, probably following infection of the ducts; hepatitis following the damming back of the bile in the liver; impairment of liver function so that bile salts are not excreted normally into the bile; settling out of the cholesterol of the bile, in consequence, around a foreign nidus, dragging down pigment and mucin with it; further stasis and the establishment of a vicious circle.

E. R. LONG

Formaldehyde test in lues. D. A. JOHNSON. *J. Lab. Clin. Med.* 8, 277-8(1923).—Comparison was made of the CH_2O test of Gate and Papacosta and the Wassermann reaction in 100 male insane patients. In 27% the Wassermann was plus; in 23% the formaldehyde test was plus; in 12% the two tests corresponded; in 11% the formaldehyde test was plus with negative Wassermann; in 15% the Wassermann was plus with negative formaldehyde test. The formaldehyde test is of no diagnostic value.

E. R. LONG

Experimental contributions to the question of tuberculin immunity, especially to that of the antigenic action of tuberculin. A. WOLFF-EISNER. *Z. Immunitäts.* 35, 215-67(1922).—Treatment of healthy rabbits with preps. of killed tubercle bacilli

induced typical sensitiveness to tuberculin. Without living tubercle bacilli it was possible to call forth the typical pathological-anatomical picture of tuberculosis, including tuberculin hypersensitivity. An immunization is therefore possible, contrary to the usual claim, without the use of living tubercle bacilli. Tuberculin is to be considered a foreign protein (endotoxin), capable like other foreign proteins of stimulating the production of lytic antibodies in the body. The tuberculin reaction is classified correctly among the anaphylactic reactions.

E. R. LONG

The sedimentation velocity of blood corpuscles in pulmonary tuberculosis. HANS POINDECKER AND KARL SISS. *Wiener klin. Wochschr.* 35, 971-3, 997-8(1922).—From an extensive study of the subject the authors conclude that: The sedimentation velocity (*S. V.*) value for normal individuals varies considerably, but is fairly const. for any given normal individual. An elevation in the *S. V.*, after the exclusion of other phys. causes, indicates pulmonary disease with tissue breakdown or with exudative effusion, but is of on definite value as far as the specificity or kind of lung involvement are concerned. The test is to be used with caution in the diagnosis of predominating fibrous forms of tuberculosis. The higher values are definitely indicative of the activity of the infection. The test permits the differentiation of incipient phthisis from benign apical tuberculosis. The continuous application of the test in the study of a case of pulmonary tuberculosis facilitates the evaluation of the activity, progress and prognosis of the disease. The detn. of the *S. V.* is easily carried out in practice and should not be omitted in the study of any pulmonary disease, but it is only of value when carried out with great care, and when other interfering irrelevant factors are accounted for. The technic is described in detail.

W. A. PERLZWEIG

Measurement in variations of the specific gravity of serum as a method for demonstration of the Abderhalden reaction. E. KRASNUSCHKIN. *Fermentforschung* 6, 241-7 (1922).—The method of Hammerschlag is used for detg. the sp. gr. by detg. the proportion of CHCl_3 and C_6H_6 that corresponds to the sp. gr. of a drop of blood. Results are obtained which correspond to those obtained by the more complicated dialysis method and which support the opinion that this reaction is sp. The method is recommended for clinical purposes because of its simplicity and because only a few drops of blood are needed so that it constitutes a "Micro-Abderhalden" method.

H. G. WELLS

Catalase content of the blood in carcinoma. ZERNER. *Z. Krebsforschung* 19, 263-7(1922).—The catalase activity of the blood is distinctly reduced in patients with carcinoma. In anemia there is a fall of the blood catalase in proportion to the number of erythrocytes but in cancer the decrease in catalase is often greater than corresponds to the reduction in erythrocytes. In pernicious anemia the catalase index (ratio of catalase to erythrocytes) is, if anything, increased, but in anemia from other disease, the catalase index is not altered, hence the existence of a low catalase index may be of diagnostic value in cancer. In early cancer, however, the catalase index is usually normal.

H. G. WELLS

H—PHARMACOLOGY

ALFRED N. RICHARDS

The influence of small amounts of thyroïdin on the red blood picture. H. ZONDEK. *Deut. med. Wochschr.* 48, 1033-4(1922).—Small amts. of thyroïdin lead to an increase of hemoglobin and the number of red blood cells.

S. AMBERG

Experience with "Kamillosan." A new use of chamomille. H. KOWALZIG. *Münch. med. Wochschr.* 69, 49-50(1922).—Kamillosan is a prepn. obtained from the flowers of *Matricaria chamomilla*. Clinical report about its beneficial action particularly in dysentery.

S. AMBERG

Yatren with special reference to two cases of acute yellow atrophy of the liver after its intravenous injection. ZIELER AND G. BIRNBAUM. *Münch. med. Wochschr.* 69, 604-6(1922).—Yatren is iodoxyquinolinesulfonic acid. S. AMBERG

Saccharin intoxication. P. HEILMANN. *Münch. med. Wochschr.* 69, 968-9(1922).—A 9-year-old boy took in an afternoon 200 saccharin tablets contg. 14 g. sol. saccharin equal to 3.5 g. refined saccharin. The rest was NaHCO_3 . There was a delirium and an enormous urticaria with big blisters contg. coagulated serum. Recovery. S. AMBERG

The action of chloretone on the irritability of the parasympathicus. E. LOUIS BACKMAN. *Arch. néerland. physiol.* 7, 518-22(1922).—Chloretone, which is used quite generally for preserving adrenaline and pituitrin, produces a marked decrease of the irritability of pilocarpine for small intestines of the rabbit suspended in Tyrode soln. R. BEUTNER

III effects from phenolphthalein medication. C. SCHELENZ. *Pharm. Zentralhalle* 63, 637-8(1922).—A discussion of the phenomena observed in several typical cases. W. O. E.

The action of atropine on the pulse and blood pressure. O. PLATZ. *Z. ges. expth. Med.* 28, 81-9; *Klin. Wochschr.* 1, 2001(1922).—Atropine in small doses up to 0.5 mg. intravenously and subcutaneously causes a slowing of the pulse. Larger doses ultimately accelerate the pulse. There is a tendency toward a fall in blood pressure following intravenous injection of atropine. E. B. FINK

Experiences with trichloroethylene in cases of trigeminal neuralgia. KURT MAGUNNA. *Klin. Wochschr.* 1, 618-9(1922).—The inhalation of C_2HCl_3 had a beneficial effect in about 50% of cases of true trigeminal neuralgia. About 25% of the cases were permanently cured. The compd. was also used successfully in alleviating the distress that is occasionally felt after lumbar puncture. MILTON HANKE

Novasural as a diuretic. F. KULCKE. *Klin. Wochschr.* 1, 622-5(1922). M. H.

Experiences with yatren, especially concerning the dangers associated with its intravenous application. HANS MICHAEL. *Klin. Wochschr.* 1, 1153-6(1922).—Yatren (iodoxyquinolinesulfonic acid) is a valuable local antiseptic. Its intravenous administration may, however, lead to severe icterus and inflammations of the mucous membranes of the intestinal tract. Cases of gonorrhea show no improvement when they are treated intravenously with aq. solns. of pure yatren. MILTON HANKE

Tolerance and acquired tolerance of the (embryonic) mesenchyme cells in tissue-cultures for copper sulfate and sodium arsenite. J. L. WILSON. *Bull. Johns Hopkins Hosp.* 33, 375-7(1922). A. P. LOTHROP

The influence of water deprivation, pilocarpine, and histamine upon changes in blood concentration in the rabbit. F. P. UNDERHILL AND S. C. ROTH. *J. Biol. Chem.* 54, 607-15(1922).—The rabbit was chosen as the expth. animal because it is more or less refractory to various influences to which the dog is susceptible and thus extends the range of factors involved in regulation of H_2O balance. "Complete deprivation of H_2O leads to blood concn., the level attained lying within the limits of safety suggested by previous investigations (125% of the normal value). High blood concns. induced by H_2O deprivation rapidly fall to normal levels upon administration of H_2O . Under the influence of pilocarpine blood concn. is markedly increased but quickly returns to the normal level (within 2-3 hrs.). Pilocarpine action superimposed upon prolonged H_2O deprivation causes exceptionally high blood concns. (136% of the normal value) which rapidly attain the normal upon H_2O administration. In the rabbit histamine fails to produce blood concn. Little or no change is to be observed except perhaps an insignificant lowering. These observations with histamine are quite unlike those previously obtained under similar expth. conditions with dogs." A. P. LOTHROP

Studies of the biological action of strontium. GIOVANNI CAGNETTO. *Atti ist. Veneto* 79, 231-48, 249-66(1919-20).—Sr given to various young animals causes depression of growth and also affects unfavorably the skeletal structures. S. M.

The diameter of red cells during deprivation of water. TH. SARAGEA. *Compt. rend. soc. biol.* 87, 623-5(1922).—S. finds exptl. proof showing that the no. and the diam. of the red blood cells may undergo temporary changes under physiol. conditions. Following the administration of Na_2SO_4 to rabbits and to man there has been an increase in the diam. S. MORGULIS

Comparative action of certain purgatives on cholesterolemia. M. LOEPER AND E. M. BINET. *Compt. rend. soc. biol.* 86, 903-4(1922).—Expts. with Na_2SO_4 , rhubarb and phthalein show that the first is the most effective agent in reducing the cholesterol content of the blood. S. MORGULIS

Adrenaline and liver glycogen. DOYON. *Compt. rend. soc. biol.* 87, 598(1922).—A note claiming priority in the discovery that the liver glycogen disappears under the influence of adrenaline and also of pilocarpine. S. MORGULIS

Action of carbonic acid on gastric motility and passage through the pylorus. P. CARNOT AND W. KOSKOWSKI. *Compt. rend. soc. biol.* 87, 613-6(1922).— H_2CO_3 introduced into the stomach or subcutaneously causes a notable increase in the gastric contractions and evacuation through the pylorus. This effect can be abolished by a preliminary atropine injection. The effect is therefore believed to be produced in the gastric and pyloric musculature by way of the parasympathetic. These results of exptl. studies correspond to the utilization of carbonated waters therapeutically. S. M.

Influence of glucose on the adrenaline effects on the isolated heart of the rabbit. E. CLAES. *Compt. rend. soc. biol.* 87, 783-5(1922).—The expts. were made on isolated rabbit hearts suspended in a moist chamber at 37° . The heart was irrigated with Locke soln. while the adrenaline was passed through the coronary circulation. The heart is extremely sensitive to adrenaline, responding to 0.000625 mg. dissolved in 1 l. of Locke soln. The adrenaline effect manifests itself in 3 phases. First, there is an initial depression characterized by a diminution in both rhythm and strength of the contraction. This is rapidly superceded by the next phase of excitation which is more or less protracted according to the heart and the dose of adrenaline. In this phase both the amplitude and the rate of contraction are increased. There is also frequently an auriculoventricular dissoc. which results from the stimulation of the cardiac sympathetic. Finally there is a phase of depression which sets in at variable times but differs from the initial phase in that the rhythm is not affected simultaneously with the strength of the beat, being depressed much more slowly. By injecting the rabbits with glucose for 3 days prior to the isolation of the heart the excitation phase persists longer and is not followed by a depression. From this it is concluded that the depression is not due to an exhaustion of the nervous system but to the fatigue of the myocardium. S. MORGULIS

The passage of adrenaline from the cerebrospinal fluid into the general circulation. I. I. NITZESCU. *Compt. rend. soc. biol.* 87, 818-20(1922).—This problem has been approached from the point of view of the changes in blood sugar and in leucocyte count which an injection of adrenaline into the cerebrospinal canal would produce. Since these are affected in a very definite manner by subcutaneous adrenaline injections, the blood changes were used as an index of the passage of the adrenaline into the blood. Into 2 dogs weighing, resp., 13.5 and 7.5 kg. N. injected 0.7 and 0.4 cc. of adrenaline. A marked hyperglucemia developed which attained a max. in 4-6 hrs., and about 12 hrs. passed before the normal level was reestablished. Also the leucocyte count showed a very marked increase which reached a max. in about 5-7 hrs., returning to normal in 24 hrs. In one instance N. found that the no. of leucocytes were trebled. The differ-

ential count also shows interesting changes, the % of polynuclear cells increasing while that of the mononuclears diminishes, and these changes follow parallel to the alteration in the total count. S. MORGULIS

Curare-like action of snake venoms on frogs. B. A. HOUSSAY AND S. PAYR. *Compt. rend. soc. biol.* 87, 821-3(1922).—Snake venoms from many different species were tested for their curare-like action on the frog muscle. The expts. are difficult to perform owing to the fact that heart paralysis is frequently also caused by the poison. Following a subcutaneous injection fibrillation of the muscles commences, which does not stop even upon sectioning the nerve. Immediately after the injection the irritability of the muscle is diminished. A comparison of the doses of venom necessary to produce the curare-like effect upon the frog muscle and to cause *in vitro* hemolysis of dog blood cells shows considerable differences in the amts. required, which leads to the conclusion that the factors responsible for the hemolytic action are different from those causing the paralysis of the muscle. S. MORGULIS

Action of the snake venom on the isolated nerve-muscle preparation. B. A. HOUSSAY, J. NEGRETE AND P. MAZZOCCO. *Compt. rend. soc. biol.* 87, 823-4(1922).—The paralytic action of the venom is peripheral. Studying the effect of immersion of either nerves or muscles into Ringer soln. and Ringer soln. contg. the venom, it has been found that the former is not affected while the muscle becomes weak and then loses its irritability. The muscle remains contracted and shows fibrillation. The muscle swells noticeably in the Ringer soln. contg. the venom, and the swelling is stronger the more powerful the venom and the greater its hemolytic activity. Similar effects could be produced in the muscle by treating it with lysocithins prepd. from the yolk of egg, and these effects could be neutralized with cholesterol. The venoms are therefore supposed to act directly upon the lipoids of the muscle and produce hemolytic products, similar to the lysocithins, which greatly increase the imbibition of water and thereby cause contracture, curarization and then loss of irritability. The effect is thus thought to be occasioned by changes in the permeability of the muscle cell wall. S. M.

The influence of snake venoms on the heart. M. A. MAGENTA. *Compt. rend. soc. biol.* 87, 834-5(1922).—The venoms from 15 different snakes were examd. for their action on the isolated frog heart. Subcutaneous injection of the venom brings on more or less quickly a diminution of the no. of beats, a weakening of the heart and finally arrest in diastole or very rarely during the initial stage of systole. The cardiac paralysis precedes the curarization of the striated muscles. Immediately after the addn. of the venom to the Ringer soln. there is a marked acceleration (not with very strong venoms) and stronger beat in the isolated heart; the ventricles, however, soon begin to contract feebly and the auricles dilate. The beats become gradually slower, the A-V rhythm is dissociated, and finally the ventricle stops usually in systole. The different venoms in concn. of 1:1000 have different degrees of cardiotoxic action: from *Naja tripudians* the effect is obtained in 7 min. and from *Ancistradon blomhoffi* in 117 min., these representing the 2 extremes. The response to a Faradic current increases immediately after treatment with the venom, but gradually grows less active as the ventricular beat also dies away. The refractory period in that state is greatly prolonged. The venom evidently acts directly upon the cardiac muscle. S. MORGULIS

Anesthesia of the dog through the intravenous injection of a mixture of alcohol-chloroform-physiological salt solution. HENRY CARDOT AND HENRI LANGIER. *Compt. rend. soc. biol.* 87, 889-92(1922).—The mixt. is made up from 100 g. water, 0.8 g. NaCl, 0.6 g. CHCl₃ and 8 g. 95% alc. Of this mixt. 5 cc. per kg. of body wt. is injected into the dog which was previously given morphine. Very profound and complete anesthesia is produced almost instantaneously. The method is recommended for all operative procedures for which a deep but brief anesthesia is required. S. MORGULIS

The utilization of the green lizard (*Lacerta muralis*) for the physiological assaying of poisons. SEVERIN ICARD. *Compt. rend. soc. biol.* **87**, 893-5(1922).—The lizards cast off the tail easily, and it has been found that the severed tail will continue to contract and wiggle for about 45 min. These movements are entirely independent from the central nervous system. It is possible completely to anesthetize the animal and by applying hot pincers to cause contraction of the tail while the rest of the body remains inactive. Also under the influence of curare the tail musculature is unaffected and can be stimulated to activity either by means of mech. stimulation applied to the trunk or through the injection of muscle excitants (veratrine or BaCl_2). The peculiar behavior of the lizard tail has been utilized to study whether various substances are nervous or muscular stimuli. With poisons which are nerve paralyzers it was impossible to provoke any response of the trunk muscles but the tail would respond to stimulation. With poisons which are muscle paralyzers no movements were obtained either in the trunk or in the tail. When nervous system stimulants were used without an anesthetic there were spontaneous and convulsive movements of the entire body, which stopped in the tail portion when this was sepd. from the trunk; with an anesthetic there were no spontaneous movements of the tail. With muscle stimulants, without anesthesia, there were convulsive and spontaneous movements of the whole body which persisted also in the severed tail; with anesthesia, there were spontaneous and convulsive movements of the tail.

S. MORGULIS

Influence of some mineral salts on the amylolytic action of pancreatin. H. DAFONSECA. *Compt. rend. soc. biol.* **87**, 1033-5(1922).—A measured quantity of pancreatin was mixed with a potato-starch paste made by boiling 0.5 g. in 50 cc. of water. The mixt. was then kept for a definite time at 40°. In other expts. the conditions were exactly the same except that a certain amt. of the different salts was also added to the mixt. The conclusion reached was that NaCl and CaCl_2 exercise a strong stimulating effect upon the fermentation of the potato-starch paste with pancreatin; the ZnCl_2 and ZnSO_4 were found to have an inhibiting action, while Na_2SO_4 is entirely without effect.

S. MORGULIS

New experiments on the influence of adrenaline on the hypertension produced by splanchnic stimulation. B. A. HOUSSAY AND A. P. MARCONI. *Compt. rend. soc. biol.* **87**, 1049-52(1922).—From expts. on dogs the authors conclude that the stimulation of the splanchnic nerve produces a discharge of adrenaline which causes an increased arterial blood pressure and a vasoconstriction in the denervated limb. These effects manifest themselves in animals whose circulation has been reduced to that of the head, thorax, the adrenals and one limb. This vasoconstriction and rise in blood pressure were not observed if the adrenal (lombocapsulaire) vein was at first clamped off, but did appear as soon as this was released. The same results are found in dogs receiving a continuous adrenaline injection.

S. MORGULIS

Strychnine and the phenomena of inhibition. FRÉDÉRIC BREMER. *Compt. rend. soc. biol.* **87**, 1055-7(1922).—The reciprocal action of antagonistic muscles which involves the stimulation of one and the inhibition of the other of the pair is offset by small doses of strychnine. Sherrington has shown that under the influence of strychnine (also of tetanus toxin) the inhibitory effect is changed to a stimulating effect. B. maintains that this inversion of the inhibitory effect of stimulation is due to the fact that strychnine has a selective action on the motor fibers in the mixed fiber nerves.

S. MORGULIS

Action of arecoline on the sinus, auricles and ventricle of the frog heart. C. HEYMANS. *Compt. rend. soc. biol.* **87**, 1062-4(1922).—Arecoline, the alkaloid extd. from *Semen arex*, when injected subcutaneously or intravenously into a no. of different organisms, produces symptoms which indicate that the substance belongs to the class of para-

sympathetic stimulants. Its action is suppressed by atropine. Large doses bring about arrest of the sinus, auricles and ventricle, through vagus stimulation. Small doses arrest the sinus and the auricles but the ventricle is not affected. Though arecoline has no direct ventricular effect it suppresses the effects of the Stannius ligature. In the presence of an excess of Ca the parasympathetic excitation of the heart through arecoline can be reversed owing to the hyperexcitability of the sympathetic endings produced by the Ca. S. MORGULIS

The value of phenylethylmalonylurea in the treatment of epilepsy. L. CHEINISSE. *Presse med.* 30, 42-3(1922). W. A. PERLZWEIG

Anti-shock medication by means of concentrated glucose solution. DUHOR. *Presse med.* 30, 61(1922).—D. prevented shock following arsenical treatment in susceptible cases by administering novarsphenamine dissolved in 50% glucose soln. He claims that the presence of the concd. sugar soln. prevents flocculation of As compds. in the blood. W. A. PERLZWEIG

Calcium chloride in cardiac medication. L. CHEINISSE. *Presse med.* 30, 81-2 (1922).—C. reviews the literature and points out that CaCl_2 is of benefit in cases of cardiac decompensation with edema, where the diuretic effect of the salt is utilized, for cardio-renal conditions with hypertension and in cases of gastro-intestinal disturbances following prolonged digitalis treatment. W. A. PERLZWEIG

Precautions in the use of quinidine in cardiac therapy. L. CHEINISSE. *Presse med.* 30, 126-7(1922).—A short review of dosage, frequency of administration, contraindications, etc. W. A. P.

The use of sodium citrate in vascular diseases. L. CHEINISSE. *Presse med.* 30, 258(1922).—A review. W. A. PERLZWEIG

Dangers in the use of pituitary extract in obstetrics. L. CHEINISSE. *Presse med.* 30, 302-3(1922).—A review. W. A. PERLZWEIG

Calcium salts in the treatment of asystole. D. DANIELOPOLU, S. DRAGANESCO AND P. COPACEANU. *Presse med.* 30, 413-4(1922).—Ca salts are not superior to digitalis and strophanthin in the treatment of asystole. They have the disadvantage of increasing the coagulability of the blood. W. A. PERLZWEIG

Therapeutic applications of adsorption (blood charcoal). L. CHEINISSE. *Presse med.* 30, 602-3(1922). W. A. PERLZWEIG

Innervation of chromatophores. R. H. KAHN. *Arch. ges. Physiol.* (Pflüger's) 195, 337-60(1922).—The changes brought about in the chromatophores of the frog skin by such substances as adrenaline, nicotine, and pilocarpine lead to the conclusion that these cells are under the control of a double innervation. G. H. S.

Choline as the hormone of intestinal motion. VII. Choline content of the gastro-intestinal tract in hunger and after morphine. K. ARAI. *Arch. ges. Physiol.* (Pflüger's) 195, 390-409(1922); cf. *C. A.* 16, 2931.—In cats the choline content of the stomach and of the intestine is not altered by starvation for periods of 17, 48, or 96 hrs. The administration of morphine (6 mg. per kg. of body wt.) caused a decrease in the choline of the stomach; 20 mg. markedly diminished the choline content of both the stomach and the intestine. One mg. per kg. had no effect whatever. G. H. S.

Physiological and pharmacological studies of respiration in cold-blooded animals. F. F. WERNER. *Arch. ges. Physiol.* (Pflüger's) 196, 83-91(1922).—The effects of various substances—urethan, chloral hydrate, strophanthin, strychnine, and atropine—upon the coördination of respiratory movements were detd. in the frog. The diff. substances induce more or less distinctive modifications of either the inspiratory or the expiratory phase, or of both. G. H. S.

The porphyrin of urine in lead poisoning. O. SCHUMM. *Z. physiol. Chem.* **119**, 139-49(1922).—The porphyrin present proved on spectroscopic examn. to be cotoporphyrin (principal bands in 25% HCl at 593.4 and 550.6). R. L. STEHLÉ

I—ZOÖLOGY

R. A. CORTNER

Chemical study of *Ceroplastes bergi* (fam. Coccidae) and its secretion. E. E. PRAGGIO. *Anales asoc. quim. Argentina* **10**, 178-88(1922).—This scale-like insect, common in Argentina, infests various plants, including the fig and peach. Twigs are often completely covered with a crust consisting of the insects and their secretion. The secretion consists mainly of a wax sol. in CHCl_3 but not in MeOH, and contg. a small amt. of a red dye similar to carmine. The wax has d_{44} 0.9425, m. 65-7°, I no. 97, sapon. no. 103. Much exptl. and analytical data are given. L. E. GILSON.

Respiratory exchange in fresh water fish. IV. Further comparison of gold-fish and trout. J. A. GARDNER AND GEORGE KING. *Biochem. J.* **16**, 729-35(1922); cf. *C. A.* **9**, 108, 825; **16**, 3689.—Measurement of the O tension at the asphyxial point at various temps. in the case of trout and gold-fish, and a detn. of the glycogen content of both fish, give results that indicate a low level of metabolism of gold-fish as compared to trout. V. EELS. *Ibid* 736-8.—Eels also live at a much lower plane of metabolism than trout. BENJAMIN HARROW

Observations on the melanophores of the frog. K. UYENO. *J. Physiol.* **56**, 343-52(1922).—When a severed frog foot is placed in O_2 there is complete concn. of the pigment in the cutaneous melanophores in less than 1 hr.; in air concn. was complete in 2 hrs. In CO_2 there was moderate dispersion in most of the cells lasting many hrs. O_2 and CO_2 appear to have a similar action on the deep lying melanophores, but it is very slight. J. F. LYMAN

The parthenogenetic activation of frog eggs (*Rana temporaria* L.) by hypotonic solution. R. HOVASSE. *Compt. rend. soc. biol.* **87**, 313-5(1922).—The parthenogenetic activation of the frog egg in hypotonic solns. is due to the imbibition of water by the egg colloids. This H. bases particularly on expts. in which isosmotic solns. of both electrolytes (salts) and nonelectrolytes (sucrose, urea), all with the same lowering of the f. p. ($\Delta = 0.7^\circ$), were employed. The swelling as measured by the diam. of the surrounding gelatinous membrane was greatest in pure water, and in nonelectrolyte solns. considerably greater than in the isosmotic electrolyte solns. S. MORGULIS

The toxicity of the interior medium of urodeles towards their eggs. A. WEBER. *Compt. rend. soc. biol.* **87**, 961-3(1922).—The serous fluid of the Batrachia exercises a deleterious effect upon their own eggs. This toxicity of the internal fluid can be diminished or entirely destroyed by grafting 4 eggs at 1-hr. intervals into the peritoneal cavity. This toxic effect tends to disappear also in animals kept in confinement. Expts. were performed to det. how long the loss of toxicity resulting from egg implantation into the peritoneal cavity would last. The animals were replaced immediately after the operation in a small pond to avoid the effect of confinement. When captured again about a month later (they were recognized by the healed wound on the abdomen) they were found to be free from the toxic influence. Eggs still surrounded by the gelatinous membrane were enclosed in collodion membranes of different degrees of permeability. When tightly fitting collodion membranes of slight permeability were used the eggs grafted into the peritoneal cavity of a male *Triton cristatus* remained unaffected. When, however, loose collodion membranes of large permeability were used the toxic influence of the serous fluid manifested itself though somewhat less strongly than usual. Inasmuch as the collodion membrane is supposed to permit the passage of albumin

but not of globulin, and because the serous fluid exercises the same action as the blood W. thinks that the substance which alters the egg of the urodeles and prevents their development may perhaps be a globulin. S. MORGULIS

A critical study of the facts of artificial fertilization and normal fertilization. J. GRAY. *Quart. J. Microsc. Sci.* 66, 419-37(1922). CHAS. H. RICHARDSON

The structure of the alimentary canal and its enzymes in the bee (*Apis mellifera* L.). E. N. PAVLOVSKY AND E. J. ZARIN. *Quart. J. Microsc. Sci.* 66, 509-56(1922).—The stomach (mid intestine) of the worker and drone contained catalase, amylase, invertase, lipase, pepsin, trypsin, and rennin. Inulase, lactase and emulsin were absent. Catalase was found in the rectum, but was subject to seasonal variation. From triturated stomachs, catalase decreased in the exts. on standing, while from whole stomachs it increased. Glycerol had a repressive influence on invertase. Methods for the prepn. of exts. and for testing their activity are given; also other facts of physiol. interest.

CHAS. H. RICHARDSON

Factors influencing the occurrence of alate forms in certain Aphididae. W. H. BRITAIN. *Proc. Acadian Entomol. Soc.*, No. 7, 7-29(1922).—Crowding seems to be the most important factor in the production of winged forms; starvation and $MgSO_4$ also appear to have an influence. Cf. Haviland, *C. A.* 16, 1465; Shinji, *C. A.* 12, 2098.

CHAS. H. RICHARDSON

Chemotropism of mosquitoes. W. RUDOLFS. N. J. Agr. Expt. Sta., *Bull.* 367, 23 pp.(1922).—Expts. on the causes of the attack of man by female *Aedes sollicitans* and *A. cantator* showed that perspiration, blood, urine, and sebaceous secretion of man or the cow were unattractive. Some of their constituents and decompn. products, *i. e.*, phenylalanine and hemoglobin, were decidedly attractive. Several amino acids influenced the activity of mosquitoes or induced them to suck. CO_2 and NH_3 , ultimate decompn. products of the human body, induced mosquitoes to stab and exhibit other manifestations of activation. A combination of CO_2 , NH_3 , a temp. of 35-37° and moisture (to simulate human breath) was highly activating. These stimuli, all produced by the human body, play an important role in the attraction of mosquitoes to man.

CHAS. H. RICHARDSON

Presence of free acid in the digestive tract of oligochetes. EDMUND NIRENSTEIN. *Arch. ges. Physiol.* (Pflüger's) 196, 60-5(1922).—Free acid was demonstrated in the digestive tracts of such forms as *Chaetogaster diaphanus* and *Stylaria lacustris*. G. H. S.

Organ substances with specific action. VIII. EMIL ABDERHALDEN AND OLGA SCHIFFMANN. *Arch. ges. Physiol.* (Pflüger's) 195, 167-98(1922); cf. *C. A.* 16, 2901.—Tadpoles of various ages were fed upon fresh thyroid with the result that changes in growth and development were less markedly modified in the younger animals than in the older. Goiter tissues were almost entirely without effect. *Bufo* tadpoles reacted but very slightly to thyroid which had been subjected to acid hydrolysis; although to this *Rana* forms did react. Diiodotyrosine and diiodotyramine induced changes similar to those caused by thyroid in both the *Bufo* and *Rana* tadpoles. Glycyl-diiodotyrosine and the Me ester of diiodotyrosine were*also active. Iodoacetyl-diiodotyrosine was inert, as was iodoacetyltyrosine, alival, and tyrosine. G. H. S.

Inorganic constituents of marine invertebrates (CLARKE, WHEELER) 8.

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Determination of the fat content of foods and soap. A simplified procedure. J. GROSSFELD. *Z. Nahr. Genussm.* **44**, 193-203(1922).—The method proposed is somewhat similar to the Schmidt-Bonzynski method for cheese and the Roesse-Gottlieb method for milk. As a solvent trichloroethylene was selected for the following reasons: It readily dissolves fats and oils and yet is almost entirely insol. in water; since its b. p. is 88°, it is not so volatile that appreciable loss of solvent takes place during extrn.; on the other hand it may be evapd. without difficulty; it is non-combustible, has a high sp. gr. and is low in cost; it does not readily form emulsions with water and such as occasionally form are easily broken by heating. The method for meat, sausage, or cheese is as follows: 20 g. are slowly heated with 20 cc. of fuming HCl in a Reichert-Meissl flask. After the mass is decomposed and the fat liberated it is cooled to 40-50° and exactly 100 cc. of trichloroethylene are introduced. Pumice stone is added and the flask is connected with a reflux condenser of the Allihn or similar type, a rubber stopper being used. The mixt. is then boiled vigorously for 5-10 min. After cooling to 30° the contents are poured into a separatory funnel and cooled to room temp. The underlying fat soln. is drained onto a dry filter. 25 cc. of the filtrate are evapd. in a weighed dish and dried at 100° for 1 hr. If *a* g. of residue are obtained of a fat of sp. gr. 0.95, the fat content in % = $(100/20) \times \{100a/[25 - (a/0.95)]\}$. In such products as cocoa and butter preliminary treatment with HCl is unnecessary. Comparisons of this method with the Soxhlet method usually showed agreement within 0.1% except in products of high fat content in which divergences of 0.3-0.5% were sometimes noted. It was found that a modification of this method was suitable for obtaining a large quantity of fat for chem. examn. A suitable quantity of the substance is extd. as above and as much of the clear filtered soln. as possible is introduced into a Kjeldahl flask, an equal quantity of water is added and the trichloroethylene is completely evapd. The mixt. of oil and water may then be sepd. by suitable means.

D. B. DILL

The chlorine content of cow and goat milk and formulas commonly used in infant feeding. W. R. Sisson AND W. DENIS. *Am. J. Diseases Children* **23**, 431-7(1922).—The NaCl content of cow and goat milk varies greatly. In cow milk the variation may be as high as 140%; in goat milk 20%. This variation is not due to a difference in salt intake. The NaCl content of formulas commonly used in infant feeding varies greatly.

S. AMBERG

The pasteurization process and its effect on the vitamin content of milk. A. B. MACALLUM. *Agr. Gazette Canada* **9**, 524-7(1922).—A review.

F. C. COOK

A rapid method for the determination of salt in oleomargarine and butter. F. F. FLANDERS. *Ind. Eng. Chem.* **15**, 181(1923).

E. J. C.

The margarine industry of France. A. GUILLAUME. *Bull. sci. pharmacol.* **29**, 630-7(1922); cf. *C. A.* **17**, 596.—The compn., hygienic value, food value, and com. aspects of the problem are reviewed.

F. S. HAMMETT

The fruit of *Azelia africana*. A. DIEDRICHS AND B. SCHMITTMANN. *Z. Nahr. Genussm.* **44**, 215-6(1922).—The compn. of the seed and of the arillus, resp., of this fruit was as follows: water 8.74, 6.41%; protein 21.41, 1.77%; fat 19.32, 54.08%; carbohydrates 37.42, 34.34%; crude fiber 8.92, 2.96% and ash 4.19, 0.44%. The description and measurements of the fruit and some of the oil constns. are also given.

D. B. DILL

Food value, handling and storage of maize grain. JOS. BURYTT-DAVY. *S. African*

J. Ind. 5, 473-9(1922).—In addn. to uses and food value, acidity, moisture and shrinkage as factors in handling maize are discussed.

RUTH BUCHANAN

Corresponding investigations of white, yellow, red and violet corn. E. REMY. *Z. Nahr. Genussm.* 44, 209-13(1922).—The compn. of white, yellow, red and violet corn did not differ materially as shown by parallel analyses in 1920 and 1921. The color of red and violet corn appeared to be in the anthocyanin group while that of the yellow corn seemed to be of a flavone derivation.

D. B. DILL

Flour strength as influenced by the addition of diastatic ferments. F. A. COLLATZ. *Am. Inst. Baking, Bull.* 9, 73 pp.(1922).—The bulletin includes a historical review of diastatic enzymes and the relation of carbohydrates and protein of wheat flour to flour strength. A general discussion is given of the influence of varying conditions on diastatic activity, including the detn. of the optimum p_H for the amylase of malt flour, the influence of time of digestion on the diastatic activity of malt flour, the effect of temp. upon diastatic activity, effect of concn. of diastase on hydrolysis of starch in wheat flour, effect of increasing amt. of malt flour when digested with a const. amt. of wheat flour, the production of reducing sugars in the dough during fermentation, the detn. of proteolytic activity as measured by the fall of viscosity of flour-water suspensions when digested with diastatic preps., gas production capacity of wheat flour in relation to strength, change in H-ion concn. of fermenting dough and baking data.

RUTH BUCHANAN

Maturing flour. II. F. L. DUNLAP. *Chem. Met. Eng.* 27, 934-7(1922); cf. C. A. 16, 3136.—A description of the com. equipment for developing the optimum baking capacity of flour through treatment with a mixt. of Cl and nitrosyl chloride. Its application in milling technology is discussed.

RUTH BUCHANAN

Comparative taste tests of meat extract and yeast extract. T. SABALITSCHKA. *Pharm. Ztg.* 67, 1061(1922).—Of 43 persons tasting soups made with these 2 exts., 33 gave preference to yeast ext., and 37 in the event that the cost of this product did not exceed $\frac{1}{3}$ that of meat ext.

W. O. E.

Report of coffees from Ceylon. ANON. *Tropical Agriculturist* 58, 203-4(1922).—Chem. analyses are given of several varieties of coffee.

M. S. ANDERSON

A physical and chemical study of milo and feterita kernels. GEO. L. BIDWELL, L. E. BOPST AND J. D. BOWLING. U. S. Dept. Agr., *Bull.* 1129, 1-8(1922).—The kernels of milo and feterita and the various parts into which they may be sepd. by milling resemble the corresponding parts of corn and kafir both in their phys. characteristics and chem. compn. A comparison of the proximate constituents of the kernels of these 4 sorghums shows the possibilities of their being used as raw products in certain important com. operations having for their purpose the manuf. of starch, sirup, alc. and oil when proper machinery and processes have been devised. It has been found, however, that it would probably be impractical to use them commercially for malling purposes.

W. H. ROSS

The Bulgarian soy bean. AS. ZLATAROFF AND IW. TRIFONOW. *Z. Nahr. Genussm.* 44, 214-5(1922).—Several analyses of the Bulgarian soy bean are given and compared with the compn. of the papuda (*Phaseolus radiatus*) with which the Bulgarian soy bean is sometimes confused. The papuda was found to have only half as much protein and from $\frac{1}{10}$ to $\frac{1}{15}$ as much fat as the soy bean. The compn. of two samples of milk from the soy bean is also given.

D. B. DILL

Temperature and other factors affecting the quality of silage. A. AMOS AND G. WILLIAMS. *J. Agr. Sci.* 12, 323-36(1922).—In order to define the different types of silage which can be produced (with a view to standardize feeding expts.) and the conditions under which they are produced in the American type of tower silo, the expts.

are divided into 2 parts. The first deals with silage produced by a large no. of farmers in the Eastern Counties and elsewhere; the second describes detailed expts. at Cambridge covering a period of 5 years. The silo in the latter instance was partially or completely filled each of the 5 yrs. and a silage stack prepd. in 1918. Records of the crop as ensiled and of the silage as taken out were kept. Moisture and temp. data were obtained. The following types of silage have been differentiated and some of the conditions of their production ascertained. (a) "Sweet" dark brown silage, temp. of production 45-50°, not below 45°, produced in stack silage fully aerated, but only in thin layers (6 in.-2 ft.) in tower silos. Though palatable it generally has a low feeding value, owing to loss of nutrients through excessive heating. (b) "Acid light-brown" or "yellow-brown silage," temp. of production between 30-7° in tower silos, from crops moderately mature which have been wilted until moisture content is about 70%. This type is eaten greedily by stock and is to be commended. (c) Green "fruity" silage produced in tower silos, from crops cut in the earlier stages of maturity, *i. e.*, time of flower to half formation of the seeds, ensiled as soon as cut; temp. of production 22-34°. It is greedily eaten by stock, and is of high digestibility. It has one disadvantage: a large amt. of juice drains from the silage which must be disposed of since if allowed to spread through the yard putrid fermentation sets in. (d) "Sour" silage which may be produced from an immature and succulent crop or from a crop which has been rained upon after cutting. Cattle do not thrive upon this. (e) "Musty" silage, an infrequent type of no value.

R. B. DEHMER

The composition and food value of potato-top silage. W. ZIELSTORFF. *Mitt. deut. Landw.-ges.* 37, 693-4(1922).—Substitution of potato-top silage for beet root in the regular ration of cows did not materially alter the milk and butter yields. Fresh potato tops contain H₂O 86.02, fat 0.37, crude protein 2.04, pure protein 1.64, crude fiber 3.08, N-free extractive matter 6.55, ash 1.94, org. matter 12.05%. K. D. J.

The changes which occur during the ensilage of oats and tares. A. AMOS AND H. E. WOODMAN. *J. Agr. Sci.* 12, 336-62(1922).—The object was to det. the effect of varying the moisture content, both by wilting of the crop and by addn. of water through rain, upon the quality of silage and to det. the nature and magnitude of the chem. changes which occur when different types of silage are made, and to obtain a comparison of the fermentation losses in each case, as well as any benefits which may accrue from such fermentation. The crops used, filling of silos and sample bags and opening of the silos are described in detail. Moisture, ether ext., crude fiber, ash and N-free extractives are reported with changes in each constituent as affected by fermentation. The main conclusions are: (1) The ensiling of a fresh green crop, fermentation temp. 25°, produces a green "fruity" silage. Loss is excessive through "run-off" of sap. True protein is split up into sol. nitrogenous compds., 50% being transformed into "amides." (2) A dry crop, produced by either wilting or maturing the crop, produces an acid brown type of silage, with low loss of dry matter, with little loss through drainage, and 30% of the true protein converted into "amides." (3) Prolonged wilting and extensive rain-washing do not produce good silage, a tendency to mold being noted when this material is fermented, which results in a destruction of volatile and non-volatile org. acids. Large losses of dry matter occur; "amides," N-free extractives and ether ext. are destroyed. In good quality silage the ratio of acids to volatile bases in the extrn. is high, while in spoiled silage the volatile bases may be present in excess of the amino acids. (4) Acidic fermentation varies with the type of silage produced; lactic acid probably is not the only acid formed. (5) The increases in ether-extractable material are very variable in the different expts. and bear no relation to percentage losses of N-free extractives. (6) The crude protein digestibility of the green oats and tares (as detd. *in vitro*) is lowered during fermentation. (7) Amino acids are increased,

forming a bulk of the "amides"; volatile bases are increased consisting probably of NH_4 . (8) Results suggest that cellulose undergoes a breaking down resulting in a gain of N-free extractives with a corresponding decrease in crude fiber, which has a greater digestibility than that present in the green crops.

R. B. DREMER

Report of fodder grass trials at experiment station, Peradeniya. T. H. HOLLAND. *Tropical Agriculturist* 58, 216-23 (1922).—Chem. analyses of 11 fodder grasses are given together with expts. testing their food value.

M. S. ANDERSON

Cowpeas utilization. W. J. MORSE. *Tropical Agriculturist* 58, 92-8 (1922).—Analyses are given of cowpeas and other feeding stuffs grown in different parts of the world. Cowpea straw is especially rich in digestible nutrients; it contains protein 3.4, carbohydrate 39.1, and fat 0.7%.

M. S. ANDERSON

The detection of salt in stock feeds. H. E. GENSLE. *Ind. Eng. Chem.* 15, 158 (1923).

E. J. C.

Absorption of pepsin and HCl by foods (EFFRONT) 11E.

Bread-making. WARD BAKING CO. Brit. 186,633, Oct. 2, 1922. Substances rich in water-sol. B vitamins are substituted for equal wts. of the sugars usually employed. The substances are obtained from such by-products as rice polishings, wheat bran and the germs of cereals. Fat, some of the coloring matter, and the bitter and acrid substances are extd. with C_6H_6 , CCl_4 , etc. The materials are then mixed with 10 times their wt. of H_2O and cooked to gelatinize the starch, and on cooling to about 100°F . an infusion of 4 to 30%, preferably 10%, by wt. of barley malt or malt flour is added to effect soln. and conversion of the starches into maltose and dextrins. Instead of saccharifying by a malt infusion, a suitable acid may be used such as HCl, H_2SO_4 , H_3PO_4 , citric or tartaric acids. Glucose, dextrin, sol. proteins, and mineral salts will then be present in the product. The temp. of the mixt. is maintained at 100 – 120°F . from 2 to 3 hrs. to allow the proteolytic enzymes to dissolve a considerable proportion of the proteins. The temp. is then raised to 154°F . for 12 to 20 min. to complete the soln. of the starches, and then slowly to 170°F . during a period of about 15 min. and finally more rapidly to the b. p. to destroy the enzymes. The mixt. should be acid or made so by adding an acid. The mass is filtered and the filtrate evapd. to dryness or to a sirup-like consistency in vacuum app. From 5 to 10 lbs. of the product to 100 lbs. of flour is used. The water-sol. B vitamins may be extd. after the fat sepn., by agitating the germ with H_2O or alc. for 3 hrs. at 140°F . and then evapp. The oil and fat obtained from the fat sepn. may be used in soap manuf. after regeneration of the solvent with or without preliminary hydrogenation.

Bread. W. B. JOHNSON. U. S. 1,438,441, Dec. 12. A liquid mixt. of whole rice, wheat bran and H_2O is cooked and after partially cooling is mixed with yeast and malt sirup, permitted to ferment in liquid condition with ready escape of the gas formed, then mixed with flour, refermented as a dough mixt. and baked.

Egg mixture for foods. A. D. GREENLEE. U. S. 1,438,232, Dec. 12. Egg white is emulsified with cottonseed oil and milk or other fatty material in about the same proportion that fat is present in natural egg, to obtain a mixt. suitable for use in bakery products.

Concentrating milk or other organic solutions. D. D. PEBBLES. U. S. 1,438,502, Dec. 12. Milk or other substance of org. nature in part is heated for a short period in a heater and then passed into a vacuum expansion chamber where it is subjected to evapn. as a spray. The liquid is sufficiently heated to effect pasteurization and is re-

circulated through the heater and evapg. chamber until the desired degree of concn. is attained.

Jacketed tank for pasteurizing milk or other liquids in bulk. M. GOLDBERGER. U. S. 1,438,594, Dec. 12.

Apparatus for pasteurizing milk. K. N. SNOEN. U. S. 1,439,027, Dec. 19. A foam breaker is provided for recovering milk from foam bubbles.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

What chemical industry owes to Pasteur. L. A. FERNBACH. *J. Soc. Chem. Ind.* 41, 519-20R(1922). E. J. C.

The crisis of our (French) organic chemical industry and the national defense. A. BÉHAL, A. HALLER AND CH. MOUREU. *Rev. sci.* 60, 681-4(1922). E. J. C.

Chemical trade movements in 1922. W. G. W. *Chem. Age* (London) 7, 928-31 (1922). E. J. C.

Perkin Medal award (to Milton C. Whitaker). Impressions. A. A. BACKHAUS. *Ind. Eng. Chem.* 15, 195-6(1923). Milton C. Whitaker. A. D. LITTLE. *Ibid* 196-8; portrait. Presentation. CHARLES F. CHANDLER. *Ibid* 199-200. Acceptance. M. C. WHITAKER. *Ibid* 200-3.—Organization as the keynote of successful chem. production is interestingly discussed. Also in *Chem. Met. Eng.* 28, 100-8(1923). E. J. C.

A longer college course for engineers. F. E. TURNEAURE. *Chem. Met. Eng.* 28, 18-9(1923). E. J. C.

Chemical engineering progress in 1922. J. W. HINCHLEY. *Chem. Age* (London) 7, 924-5(1922). E. J. C.

Length of work periods on continuous-process work in the chemical industries. H. B. DRURY. *Ind. Eng. Chem.* 15, 84-5(1923).—D. enumerates many industries in the U. S. that have changed from a 12-hr. day of 2 shifts to an 8-hr. day of 3 shifts. He discusses briefly the relationship to this change of (1) production, (2) efficiency, (3) problem of wage adjustment, (4) attitude of labor, (5) labor turnover. E. G. R. A.

Colloidal chemistry and patents. JULIUS EPHRAIM. *Kolloid Z.* 31, 323-8(1922).—An address reviewing the German patent law with special consideration of the conditions under which a German patent can or cannot be obtained on a colloidal substance or the method of producing it. A. MUTSCHELDER

Photosynthesis and the possible use of solar energy. H. A. SPOEHR. *J. Ind. Eng. Chem.* 14, 1142-5(1922).—The struggle for existence is essentially a fight for the potential energies in coal, sugar, meat, etc. Man must oppose nature's tendency to revert to a condition of greatest "rundownness" with respect to energy. All other sources of energy than the sun are of little significance in this connection. This energy may be utilized directly, as in solar boilers and engines, but no real advance has been made in this direction. It may be utilized indirectly through photosynthesis, as in growing plants. Agriculture is wasteful as a means for storing up solar energy. More-over the annual av. corn crop of the U. S. A. would only give alc. equiv. to the fuel value of the gasoline used in 1920. Nor is the production of fuel from cellulose a promising prospect. But nature has worked out a method for utilizing solar energy, through photosynthesis, and scientists must learn to compete with her, rather than to imitate her. Perhaps the best way to attack the problem would be through a coöperative organization by which information from various allied scientific and engineering fields

could be collected and focused on the changes taking place in the process of photo-synthesis.

W. C. EBAUGH

The pumping of liquids in chemical plants. C. S. ROBINSON. *Ind. Eng. Chem.* **15**, 33-8(1923).—R. covers briefly the construction, design and field of usefulness of (1) reciprocating pumps, (2) centrifugal pumps, (3) rotary or gear pumps, (4) blow-cases, (5) air lifts, and (6) siphons. A table gives the material to be used in constructing pumps for handling 133 different com. liquids.

E. G. R. ARDAGH

Control of industrial processes by light-sensitive means. LLOYD LOGAN. *Ind. Eng. Chem.* **15**, 40-3(1923).—This method of automatically controlling industrial processes is a hitherto comparatively neglected one. The bolometer, radiomicrometer and the thermopile are non-selective. On the other hand, there are the selenium cell, the alkali-metal cell and the thalofide cell, sensitive only to a limited range of wave lengths. L. discusses the means of applying the above 3 selective cells to the checking and maintaining within certain limits of the following characteristics of the intermediate and final products: (1) quantity of product or number of production units, (2) form or shape of product, (3) quality of product, (a) chem. compn., (b) phys. properties.

E. G. R. ARDAGH

What is wet steam? ANON. *Chem.-Ztg.* **46**, 1104-5(1922).—The popular conception is that wet steam contains strikingly large quantities of water as liquid, which cause water-hammers, etc., in the steam system; but technically it may be considered also as steam with even small amts. of liquid water suspended in it. Water in the form of mist or of gross particles is sucked out of the boiler with escaping steam, and carries with it the alkali or other solids contained in the boiler feed water. Even a superheater will not completely vaporize this liquid water, as it assumes the spheroidal state and passes through unchanged. Such water is later removed from the steam system by traps, and is often erroneously called "condensate." Water so carried causes diminished efficiency of steam, utilizes a superheater as an evaporator, makes the use of a large no. of traps necessary, corrodes engine parts, forms deposits of scale or dust, increases lubricating expense, prevents accurate steam measurements, etc. Could it be eliminated a saving of 5-20% in coal alone would result. It is claimed that a heat-recoverer, "Gestra," made by Gustav F. Gerdtts, Bremen, prevents these troubles by the application of a new method. Steam is divided into 2 streams before leaving the boiler, each of these subdivided into two angular jets which impinge on each other so that the water and steam are sep'd. so thoroughly that they have no opportunity to mix again. The water falls back into the boiler, thus conserving its heat. As superheaters receive only dry steam their efficiency is increased as much as 50%, and it is claimed that savings of 5-20% in coal are effected.

W. C. EBAUGH

Ammonia as a refrigerant. W. H. MOTZ. *Can. Chem. Met.* **6**, 260-4(1922); 7, 7-11(1923).—The paper presents a detailed study of the fundamental data relative to all factors to be considered in the operation of liquid NH_3 refrigerating systems. The calcs. cover the range from -40°F. to $+40^\circ\text{F.}$ (at 5°F. intervals) for the temp. of the sat'd. vapor in the evaporator, and the range from 60°F. to 110°F. (at 5°F. intervals) for the temp. of the liquid NH_3 . The results are embodied in 12 tables: (I) *Refrigerating effect of NH_3 , B. t. u. per lb.* (II) *Pounds of NH_3 per min. per ton of refrigeration* (the com. unit of refrigeration). A ton of refrigeration is the quantity of heat required to melt 1 ton of pure solid ice into water, from and at 32°F. This is 288,000 B. t. u. The removal of this amt. of heat per 24 hrs. may be termed 1 ton of refrigerating power. (III) *Theoretical displacement of compressor, cu.ft. per min. per ton refrigeration.* (IV) *Iditto, in cu. in. per min.* (V) *Volumetric efficiencies due to superheating for vertical single acting compressors.* (VI) *Factors for calcg. volumetric efficiencies due to clearance.* (VII) *Actual displacements of vertical single acting compressors,*

cu. in. per min. per ton refrigeration. (VIII) *Mean effective pressures of NH₃, lbs. per sq. in.* (IX) *Theoretical indicated $\frac{B}{T}$ per ton of refrigeration.* (X) *Actual indicated $\frac{B}{T}$ per ton refrigeration for vertical single acting compressors.* (XI) *Heat removed in condenser, B. t. u. per min. per ton refrigeration.* (XII) *Gals. of condenser water per min. per ton refrigeration.* M. gives also an abridged table of the properties of NH₃ taken from the U. S. Bur. of Standards figures.

E. G. R. ARDACH

Résumé of impact testing of materials, with bibliography. H. L. WHITTEMORE. *Proc. Am. Soc. Testing Materials* 22, Pt. II, 6-36 (1922). **Impact tests of metals.** D. J. McADAM, JR. *Ibid* 37-54. **Impact tests of wood.** T. R. C. WILSON. *Ibid* 55-73. **Impact tests on road materials.** E. B. SMITH. *Ibid* 74-7. **Résumé of American practice in notched bar impact tests of metals.** C. L. WARWICK. *Ibid* 78-99. **Review of the work on impact testing done by the British Engineering Standards Association.** T. D. LYNCH. *Ibid* 100-3. **Measurement of pressure caused by impact.** C. E. MARGERUM. *Ibid* 104-16. **Measuring forces in impact.** ARMIN ELMENDORF. *Ibid* 117-23. **Measurement of the force of impact by means of the elastic stretch of a steel bar.** H. F. MOORE. *Ibid* 124-7. **Significance of the impact test.** F. C. LANGENBERG AND N. RICHARDSON. *Ibid* 128-36. **General discussion.** *Ibid* 137-49.—A symposium.

E. J. C.

The theory of lubrication. W. B. HARDY. *Brit. Assoc. Advancement of Sci., 4th Rept.* 1922, 185-203; cf. C. A. 16, 2187.—The theory of external or superficial friction, standing "where Coulomb left it in 1781, accepts accidental inequalities of the surfaces as sufficient cause." Sensible asperities sometimes decrease friction; *e. g.*, that of ground glass is less than that of optically ground plate glass. The reason that friction varies with the pressure is that the cohesion of molecules across the interfaces of slip depends upon the pressure; for there is usually a "greasy" or liquid layer adsorbed at the interfaces. "Friction is the sum of the resistances offered by all the mols. about the interface to translation and to rotation. . . . As the [tangential] traction increases, the strain reaches a limit which is a true yield point, and slipping occurs. The difference between this and the yield of continuous solids lies in the fact that it is usually confined to one plane owing to the excessive heterogeneity of the system along the normal to the interface. The yield point marks the change from static to kinetic friction and the equality between the two frictions, when it obtains, means simply that the state of strain, that is the reaction to the traction, is the same in both. When the friction is raised above a certain amt. by cleaning the faces, the mols. are displaced beyond the elastic limit and part of the energy is absorbed in producing a mol. configuration of greater potential energy. The surfaces are then said to have 'sleazed.' The change in mol. configuration may be observed directly in some cases. If, *e. g.*, clean faces of glass in contact are moved past each other, tracks are left which are permanently doubly refractive." Lubrication is a special case where a composite surface results from the orientated adsorption of mols., which lessens its capacity for cohesion and also its frictional resistance. Thus an invisible adsorbed film of tripropylamine depressed the coeff. of friction on a clean glass surface from 0.95 to 0.25. The adsorbed film loses its fluidity and its viscosity increases with increasing pressure. The effect of chem. constitution upon lubricating quality is evidenced by measurements of 13 alcs., 10 org. acids, and numerous other org. compds, including ring and cyclic compds, whose effect on static friction was measured with a curved polished face of Bi applied to a plane one, the coeff. of friction of the clean surfaces being 0.5. In general static friction is a function of mol. wt., but not a simple one. Fluidity of the lubricant has no const. significance, the curves for acids, alcs. and paraffins showing no break where, with increasing mol. wt. the lubricant becomes solid at the temp. of observation. The effect of change in mol. const. is discussed, as is the nature of lubrication, practically

and mathematically. Counting from one metal surface to the other, the following layers exist: (1) cryst. metal; (2) Beilby layer; (3) adsorbed layer of lubricant; (4) main layer of lubricant; (5) absorbed layer of lubricant; (6) Beilby layer; (7) cryst. metal. If the yield occurs in the metal, the lubricant is "bad."

JEROME ALEXANDER

Rope lubrication. K. M. *Seifensieder Ztg.* 49, 833(1922).—For the lubrication of transmission ropes or cables the use of wood tar (deciduous trees) is recommended or better still, the use of "goudron," an acid-free by-product of brown coal or asphalt distn.; in the latter case it should be mixed with non-drying oils to give it sufficient softness. A renewal every 3 weeks for outside use and every 6 weeks for indoors becomes necessary after previous thorough removal of the old crusts by washing with soap.

P. ESCHER

Optical method of determining the thickness of the oil film in bearings with respect to the use of lubricants. A. WETHAUER. *Petroleum Z.* 13, 1405-12(1922).—A coördinate grating is traced on the end of the shaft. A microscopic collimator is focused upon a point of this grating while the shaft is at rest and the measurement of the distance through which the instrument must be moved to focus upon the same point when the shaft is in motion shows the thickness of the oil film on the bearing. Representative photographs of such observations are shown.

D. F. BROWN

Colloid mill and the ultra-filter press (KENNEX) 1. Chemical apparatus and technical instruction (LIESCHE) 1. Importance of impurities (ALEXANDER) 2. Disperse systems in gases (GIBBS) 2.

Chemical Engineering Catalog 1922. New York: Chemical Catalog Co. Inc. 1,188 pp. \$10. Lent out to chem. engineers for one year \$2.00 per copy. Reviewed in *J. Franklin Inst.* 194, 710 (1922).

Griffiths, Hugh: **The General Principles of Chemical Engineering Design.** London: Benn Brothers, Ltd. 3s. Reviewed in *Intern. Sugar J.* 24, 603(1922).

Griffiths, Hugh: **Materials of Chemical Plant Construction: Non-metals.** London: Benn Brothers, Ltd. 3s. Reviewed in *Intern. Sugar J.* 24, 103(1922).

Peters, Fredus N.: **Applied Chemistry.** St. Louis: C. V. Mosby Co. 461 pp. \$3.50. Reviewed in *Am. J. Pub. Health* 12, 1053(1922).

Swindin, Norman: **Chemical Works Pumping.** London: Benn Brothers, Ltd. 3s. Reviewed in *Intern. Sugar J.* 24, 603(1922).

Swindin, Norman: **The Flow of Liquids in Pipes.** London: Benn Brothers, Ltd. 3s. Reviewed in *Intern. Sugar J.* 24, 609(1922).

Recovery of solvent vapors. W. RUNGE and H. A. CURTIS. U. S. 1,349,128, Dec. 19. Volatile solvents such as ether, alc., CS_2 , $CHCl_3$ or volatile hydrocarbons are absorbed from gaseous mixts. by the action of cresol and the unabsorbed gas is then brought into contact with a "tar acid salt" such as Na phenolate or cresylate to remove cresol vapors from the gas.

Recovery of solvent vapors from drying apparatus. W. K. LEWIS and W. GREEN. U. S. 1,437,980, Dec. 5. Washed flue gas is passed over rubberized fabric or other material to be dried to take up C_6H_6 or other org. solvent vapor in high concn. and the solvent is subsequently recovered by absorption and distn. from a relatively concd. soln. Creosote oil or a heavy petroleum oil may be used as the absorbent in recovery of C_6H_6 .

Treatment of liquids with gases. C. S. BRADLEY. Can. 225,821, Nov. 14, 1922. A gas which is chemically active is introduced into a liquid to produce a foam which is recovered as the desired product.

Distilling, concentrating, and drying. T. RIGBY. Brit. 180,963, Dec. 24, 1920. Brine and other liquids are concd. and *peal*, etc., is dried on the surface of rotating cylinders heated by steam and so arranged in a closed casing as to leave a central open space from which the vapor generated can readily escape so as to be used as a heating medium either in another effect of a multiple-effect app., or, after compression, in the cylinders of the original unit. A suitable app. is specified.

Lubricating oils. H. PLAUSON. Can. 227,348, Dec. 19, 1922. Tar oils are heated with superheated steam at high temp. by intense and local heating of the mixt. in a constricted space.

Fibrous insulating sheets containing shellac. G. R. COX. U. S. 1,437,094, Nov. 28. Sheets of paper impregnated with shellac are superposed upon each other between outer sheets of paper impregnated with a phenolic condensation product, with intervening sheets of untreated paper (to obtain a good bonding or union of the materials) and the superposed sheets are heated together between pressure plates. This method of forming insulating plates avoids difficulty from adhesive character of the shellac.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

Progress in water purification. A. C. HOUSTON. *Water and Water Eng.* 24, 445-50(1922). E. H.

Tastes and odors from chlorine. EDWARD BARTOW AND R. M. WARREN. *Eng. News-Record* 89, 878(1922).—Chlorinated water may have tastes other than that from excess of Cl. Further oxidation by aeration may increase rather than remove taste. The O consumed method is applicable only when taste is due to excess Cl. Presence of excess air assists odors to escape. The colorimetric method for Cl is inaccurate when phenol or cresol is present in the water. FRANK BACHMANN

Small iron removal plant for the water-works of Leroy, Ohio. A. E. KIMBERLY. *Eng. News-Record* 89, 965-7(1922).—The raw water contains 2.0 p. p. m. Fe, 64 p. p. m. CO₂, and no O. The Fe removal plant consists of an aerator, roughing filter and rapid sand filter. The roughing filter is more effective than sedimentation after aeration in coagulating the Fe. The plant removes all the Fe and CO₂, and increases the O content of the water to 68% satn. FRANK BACHMANN

An experience with air-binding of rapid filters. WM. D. HATFIELD. *Eng. News-Record* 89, 783-4(1922).—Air accumulations in the sand beds at Highland Park, Mich., reduce the period of filter-run 20-50%. Investigation showed that leaky pump glands permitted air to be sucked into the water, thereby supersatg. the water with O, which supersatn. persisted even after passing through the coagulating basins. Repairing the pumps relieved the trouble. FRANK BACHMANN

Filters for Duluth water supply considered unnecessary. H. A. WHITTAKER AND J. A. CHILDS. *Eng. News-Record* 89, 937(1922).—Filtration would only reduce the low turbidities. FRANK BACHMANN

Studies of natural purification on the Illinois River. J. K. HOSKINS. *Eng. News-Record* 89, 1078-9(1922); cf. C. A. 17, 165.—Laboratories were established at Joliet, Peoria, Beardstown, and Kampsville from the headwaters to the mouth of the Illinois River. The total bacterial counts on agar at 37° immediately below the Drainage Canal ranged from 2 to 5 million per cc. whereas in the winter months they ranged

from 100,000 to 300,000. Gelatin counts at 20° and agar counts at 37° (24-hr.) are about the same during the summer months but in winter they diverge, the agar counts becoming much smaller than the gelatin counts. A distinct decrease in bacterial pollution takes place between the outlet of the drainage canal and immediately above Peoria. At the latter point, the river is not highly polluted judging from bacterial analysis. In the upper stretches of the river the O demand exceeds the supply but just above Peoria an O balance is reached.

FRANK BACHMANN

Percentage of water pumped which produces revenue. H. F. HUY. *Eng. News-Record* 89, 944-5(1922).—By special care (precautions described) the Western N. Y. Water Co., which operates in the suburbs of Buffalo and supplies about 60,000 people, obtains revenue from about 90% of the water pumped.

FRANK BACHMANN

Pollution of streams affecting industrial uses. J. F. JACKSON. *J. New Eng. Water Works Assoc.* 36, 14-31(1922); cf. *C. A.* 16, 2945.—J. discusses the pollution of streams by industries and the effects upon the quality of the water taken by the industries from these streams.

G. C. B.

Testing sprinkling filter stone by freezing and thawing. GRANT, FULTON & LETTON. *Eng. News-Record* 89, 938-9(1922).—Tests made by alternately freezing and thawing indicated that Sioux Falls quartzite or granite is the best material for trickling filters. Limestone had disintegrated quite appreciably after exposure during 2 winters.

FRANK BACHMANN

Making separator and diffuser container blocks. R. R. LUNDAHL. *Eng. News-Record* 89, 785-8(1922).—Method of manuf. of aeration units for Milwaukee sewage works is detailed.

FRANK BACHMANN

The septic tank, a method of sewage disposal for the isolated home. H. E. MURDOCK. Montana Agr. Expt. Sta., *Bull.* 137, 27 pp.(1920).—Description of a modern septic tank and its operation.

H. W. EASTERWOOD

Fertilizing value of activated sludge. H. D. BROWN. *Eng. News-Record* 89, 885(1922).—See *C. A.* 17, 171.

FRANK BACHMANN

Treatment of tannery wastes to prevent stream pollution. F. B. BESSELIEVRE. *J. Am. Leather Chem. Assoc.* 17, 605-11(1922).—B. describes the operation of Dorr screens and clarifiers. An av. removal of 70.9% of the suspended matter of tannery sewage was effected by the combined use of screen and clarifier. From a daily flow of 423,000 gallons an av. of 19.8 tons of sludge contg. 91% water was obtained. No great success has yet attended attempts to produce a fertilizer from tannery sludge and screenings. In one instance a market was found for recovered hair. The cost of treating 423,000 gallons per day was \$3.20, of which \$1.20 went for power and the balance for labor. One million gallons per day can be treated in a plant requiring a total area of 6,330 sq. ft.

J. A. WILSON

Seattle fills land with garbage, ashes and refuse. C. L. MURRAY. *Eng. News-Record* 89, 876-7(1922).—These wastes are used to fill in land at a cost of 30 cents per ton. The garbage is covered with earth or ashes when deposited and nuisances from odors and flies have been absent. Three incinerators were abandoned because of the high cost of operation.

FRANK BACHMANN

Water supply in its relation to sewage disposal. J. C. KEITH. *J. Am. Water Works Assoc.* 10, 147-50(1923).—See *C. A.* 17, 169.

E. J. C.

Disinfection of public water supplies in its relation to public health. C. A. JENNINGS. *J. Am. Water Works Assoc.* 10, 127-38(1923).—See *C. A.* 16, 777.

E. J. C.

Cause of decrease in typhoid rate in the United States. GEO. C. WHIPPLE. *Eng. News-Record* 89, 794(1922).—Curves show changes in the typhoid rates in 2 states and 6 cities. Improvements of water and milk supplies are factors.

F. B.

Alterations and corrosions observed in cast iron water mains (BADO, BERNAOLA) 9.
Scale (SORNAY) 28.

Sterilization and purification of water. J. N. A. SAUER. Can. 228,045, Nov. 14, 1922. Water is sterilized and simultaneously purified by treating it with finely divided decolorizing C (active C of vegetable origin) contg. a very small content of mineral substance. The C has preferably been subjected to a high temp. Cf. C. A. 17, 161.

Purifying liquors contaminated with phenol. R. L. BROWN. U. S. 1,437,394, Dec. 5. Waste NH_3 still liquor or similar liquor contaminated with phenol is passed through a filter contg. peat or other humus carrying aerobic bacteria from activated sewage sludge or other phenol-destroying microorganisms which act upon the liquor and in the diln. in which it is treated maintain an approx. balance between wastage and reproduction of the microorganisms in the filter.

Purifying liquors contaminated with phenol. H. S. DAVIS and S. D. SEMENOW. U. S. 1,437,401, Dec. 5. Phenol-destroying microorganisms are developed in a humus material adapted for absorbing phenol-contaminated liquors, e. g., by aerating a spent lignite filter inoculated with aerobic bacteria from sewage sludge.

Sewage disposal plant. H. E. ELROD. U. S. 1,439,407, Dec. 19. Agitators actuated by the sewage are placed in gas vents of a sewage tank, to prevent stoppage of the vents by sewage scum.

Sewage disposal plant employing the "activated sludge" method. H. E. ELROD. U. S. 1,439,406, Dec. 19.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Modern work on soil physics. G. G. AUCHMUECK. *Tropical Agriculturist* 58, 174-84(1922).—The general principles of soil physics are discussed with special emphasis upon the effect of the presence of colloidal clay.

M. S. ANDERSON

The flocculation of soils. III. N. M. COMBER. *J. Agr. Sci.* 12, 372-86(1922); cf. C. A. 16, 3154.—Further support of earlier deductions (cf. C. A. 15, 2326) is offered from exptl. observations on (1) the flocculation of particles other than soil particles, (2) the effect of colloidal Si on the suspensibility of particles, (3) the effect of concn. on the relative flocculating powers of $\text{Ca}(\text{OH})_2$ and CaCl_2 , (4) the relative Ca-absorbing capacities of the core and of the colloidal particles, (5) the effect of heating on soils. Certain phosphates of Fe, Al, and Ca showed the same abnormal flocculation by $\text{Ca}(\text{OH})_2$ that is shown by clay. Until the $\text{Ca}(\text{OH})_2$ reaches a certain amt. its abnormal flocculating power is not manifested. This amt. is greater for a fat than a lean clay. This is in agreement with the view that the abnormal flocculation is caused by a coagulation of emulsoid matter, for such a coagulation will not become dominant until a sufficient amt. of the precipitant has been added. Absorbed Ca can be removed by dil. acid which cannot very appreciably decompose unweathered minerals. It follows, therefore, that the absorption of lime by a soil is an absorption by the soil colloids and not by the unweathered minerals. Ignition increases the amts. of Fe and Al dissolved by acid. Evidence shows that this is due to a destruction of the colloids which bind the particles together. "The effect of a partial ignition on the base-absorbing power of soils and subsoils is described and the results are claimed to be in agreement with the view that particles in the aggregate are bound together by gelatinous colloidal matter."

R. B. DREMER

The simultaneous presence of nickel and cobalt in arable soil. G. BERTRAND AND M. MOKRAGNATZ. *Bull. soc. chim.* 31, 1330-3(1922).—See C. A. 16, 3724.

E. J. C.

A modified test for sour soils. N. M. COMBER. *J. Agr. Sci.* 12, 370-1(1922).—An aq. soln. of K salicylate (5%) develops a violet color with traces of ferric salts. This reaction is applied to acid soils with the same manipulation as in the KCNS test. With acid soils a red color develops in a few min. while a yellow or brownish yellow color is developed in other soils. More concd. solns. of the reagent give a quicker reaction.

R. B. D.

The interpretation of mechanical analysis of soils as affected by soil colloids. R. O. E. DAVIS. *J. Am. Soc. Agron.* 14, 293-8(1922).—Mech. analysis does not clearly indicate the quant. distribution of the various sized mineral particles in the soil and especially in the silt and clay groups. These groups of mineral particles are made up in part of colloidal material which may be detd. by the absorption of water vapor. The major portion of the colloidal material is contained in the silt and clay groups, so that by detg. the colloid in the soil and in these two groups, information might be obtained that would show the amt. and distribution of this colloid, and as a result the correction that should be applied to the mech. analysis to show the proper amts. of mineral particles in those groups.

F. M. SCHERTZ

Analysis of soils of Pierce County. W. A. WORSHAM, JR., L. M. CARTER, M. W. LOWRY AND W. O. COLLINS. Georgia State Coll. Agr., *Bull.* 248, 36 pp.(1921).—Chem. analyses of 17 soil types occurring in Pierce County, Ga. are given and their fertility is discussed.

J. J. SKINNER

Fixation of nitrogen in Colorado soils. Occurrence of nitrates on rocks. W. P. HEADDEN. Colorado Agr. Expt. Sta., *Bull.* 277, 48 pp.(1922).—Nitrates occur universally on the face of rocks often in abundance but do not occur in the mass of rocks and are absent from the waters of deep wells and mines, but are often present in surface waters in large quantities. The occurrence on the surface of rocks is analogous to their occurrence in the surface soil. They occur on all kinds of rocks, especially coarse grained sandstone. The cementing material in this case is ferruginous and limy. These nitrates owe their formation to biological agents, in the sense that the N contained in them has been gathered from the atm. by these agents in their growth. This process is universal and intense enough to account for perhaps the largest deposits of nitrates. The same process is going on, under favorable conditions, on the stones and brick in the foundations and walls of buildings, where the max. quantities of both forms of N have been found. Fixation, to a very satisfactory extent, has been obtained in every trial but one. The max. obtained was 297 p. p. m. Nitrification is assumed as fully established, but in many instances the amt. of nitrification has been detd. and found to be as great as in soils. The quantities of NO_3 on or in the surface portions of rocks are adequate to account for their concn. in cavities, crevices and under ledges in rocks; also in the soil at the base of cliffs in protected places and in some caves.

J. J. SKINNER

Modern trend of chemical control in the fertilizer industry. H. C. MOORE. *Am. Fertilizer* 57, No. 8, 23-5(1922).—A review of the advantages which have followed the application of chem. control in H_2SO_4 acid phosphate and mixed fertilizer plants.

W. H. ROSS

Utilization of waste products for organic nitrogen. E. H. ARMSTRONG. *Am. Fertilizer* 57, No. 9, 31-3(1922).—A discussion of the com. methods of making waste materials such as hair, wool and leather available for use in fertilizers. W. H. ROSS

Nitrate fluctuation in the Gangetic alluvium and some aspects of the nitrogen problem in India. G. CLARK, S. C. BANERJEE, M. N. HUSAIN, ABDUL QUAYUM. *Agr.*

J. India 17, 463-74(1922).—The fluctuations in the nitrate content of uncropped, cultivated soil of the Gangetic plain during the cold weather season are recorded. The soil, a very heavy, stiff loam, had an av. N content of 0.0378% in the first foot and 0.0336% in the second. The amt. of N in the second ft. after a slight increase in Oct. showed no variation. The rapid accumulation of N in the first foot in Oct. during the prepn. of the land for autumn sowing is clearly brought out. The absence of nitrate formation in Sept. was due to the excess of soil moisture and the insufficient air supply. The cultivation operations in Oct. reduced the soil moisture and thoroughly aerated the soil.

RUSSELL M. JONES

The significance of mica minerals as a source of potassium for plants. V. M. GOLDSCHMIDT AND E. JOHNSON. *Norges Geol. Undersøkelse* 108, 89(1922).—(Publication No. 8 of Norwegian Governmental Raw Materials Committee.) A general review is given showing the compn. and occurrence of K silicate minerals in Norway and the availability of their K content. The distribution of biotite, muscovite, K feldspar, nephelite, and clays is shown on a map. The av. compn. of Norwegian rocks with respect to K minerals is given as follows: feldspar 15%, muscovite 5%, biotite 10%. Of these, the last two are of more importance because more widely distributed and their K content is more easily rendered available by weathering. Earlier expts. are reviewed showing that the K in mica minerals is more easily dissolved by reagents than that in feldspar, e. g., by aq. SO_3 , $\text{H}_2\text{O} + \text{CO}_2$ under pressure, NH_4Cl and BaCl_2 solns., etc. The authors record a number of their own expts. along the same line which confirm these conclusions. E. g., 0.5N HCl (cold) dissolves 19% of total K in biotite in 2 days and 58% in 1 month. Two % citric acid dissolves 24% in 1 month; the same soln. with the addn. of 2% CaCl_2 dissolves 50% in the same period. $\text{H}_2\text{O} + \text{CO}_2$ under 10 cm. water pressure dissolves 5.7% of total K in biotite in 1 month; the addn. of 2% CaCl_2 increases this figure to 18.3%. $\text{Ca}(\text{OH})_2$ dissolves 7.8% of total K in 40 days. Concd. NaCl soln. had little effect. Analytical methods for detg. K are reviewed. The Co nitrite method is favored for detg. H_2O -sol. K. Recent expts. on the extn. of K from greensand in America are reviewed. The authors conclude that the acid and salt solns. in the soil have a decided solvent action on the K in mica minerals, the H-ion concn. of such solns. being comparable with that of the CO_2 soln. used in one of the authors' leaching expts. This process is undoubtedly an important factor in the plant life of Norway. The authors suggest investigations to det. the relation between growth of vegetation, especially forests, and the amt. of mica minerals in the soil, also expts. with finely ground biotite as fertilizer. The latter might be practicable where transportation costs are not too high. Chem. extn. of K from mica minerals is not considered an economic possibility at the present prices of K. However, a study of soils with reference to their content of mica minerals would be valuable as a guide to amt. of K necessary to add in fertilizer.

S. GULBRANDSEN

Chemical changes in calcium arsenate during storage. C. C. McDONNELL, C. M. SMITH AND B. R. COAD. U. S. Dept. Agr., *Bull.* 1115, 1-28(1922).—Com. Ca arsenate in the dry powdered form manufactured for insecticidal purposes absorbs CO_2 slowly from the atm. during storage and increases in water-sol. As_2O_3 content unless it is packed in containers that are practically air-tight. The rates of these changes show a close relationship and depend largely upon the type of container in which the material is packed. The absorption of CO_2 is the first change noted. This is followed a little later by a rise in the water-sol. As_2O_3 content. CO_2 is taken up until all the Ca present in the form of the oxide or hydrate is completely carbonated, at which point the increase in water-sol. As_2O_3 also ceases in most cases. The slight changes in the chem. compn. of calcium arsenate under certain conditions of packing during long storage can be practically avoided by the use of tight sheet-metal drums.

W. H. ROSS

Report of the superintendent of the government guano islands. W. R. ZEDERBERG. *J. Dept. Agr. Union S. Africa* 5, 577-9(1922).—Approx. 8,500 tons of guano were collected from the islands of the Northern and Colonial groups during 1921. The av. compn. was: total P_2O_5 10.0%, H_2O -sol. P_2O_5 3.3%, P_2O_5 sol. in 2% citric acid soln. 9.6%, N 10.6%, K_2O 2.1%, and CaO 9.9%. K. D. JACOB

Annual report of the entomologist to the government, Punjab, Lyallpur. M. AFZAL HUSSAIN. *Rept. Operations Dept. Agr., Punjab 1920-21*, Part 2, 52-67.—Crude oil or solignum mixed with rosin, Na_2CO_3 and H_2O , and applied during the early morning hrs. of winter, was the most effective insecticide against mango hoppers. Expts. to det. the effect of superheating on the larvae of *Trogoderma khapra* in stored grain showed that at 52° the larvae were killed in 90 min. Lower temps. were not fatal, but at higher temps. the effect was much more rapid. Superheating and fumigation with CS_2 and HCN proved effective in killing larvae of *T. khapra* and adult *Rhizopertha dominica* present in wheat stored in elevators. Grain treated with a mixt. of sugar and strychnine, arsenious acid or plaster of Paris proved to be the best poison for rats, being 80 to 95% efficient. $BaCO_3$ pills and S fumigation gave lower results.

K. D. JACOB

Experiments with poisoned baits for grasshoppers. M. H. SWENK and F. E. WEHR. Nebr. Agr. Expt. Sta., *Bull.* 183, 28 pp.(1923).—For *Melanoplus bivittatus* wheat bran as a base was distinctly better than beet pulp or horse manure; fresh leaves were more attractive than bran but impractical to use on a large scale. Baits contg. arsenicals had the following order of attraction: crude arsenic (contg. 90% As_2O_3) < Paris green < As_2O_3 < Ca arsenate. Their final killing power as shown by all formulas was approx.: crude arsenic > Paris green > As_2O_3 > Ca arsenate. The rapidity of killing was: crude arsenic > Paris green > As_2O_3 > Ca arsenate > Na arsenite. However, Na arsenite, made by boiling As_2O_3 and Na_2CO_3 , was more efficient than any of the dry arsenicals. Molasses and soap seemed to reduce the attractiveness of the bait; NaCl reduced its attractiveness for young grasshoppers, but slightly increased it for old. Anise oil was repellent. Oranges and lemons increase the attractiveness; amyl acetate was about as attractive as citrus fruits and cheaper. The effect of weather and the age of the grasshoppers on their attraction to baits are discussed. A bibliography of 12 titles is appended. Cf. C. A. 13, 1512, 2954; 14, 3747; 15, 1371; 16, 1124.

CHAS. H. RICHARDSON

Improvements in the methods of preparing and using grasshopper baits. J. R. PARKER. Montana Agr. Expt. Sta., *Bull.* 148, 19 pp.(1922).—The effectiveness, cheapness and convenience of amyl acetate in grasshopper baits are shown in large scale practical work covering a 2-yr. period. NaCl is an important ingredient of the bait (cf. preceding abstr.). Data are given on the time of day to put out the baits.

CHAS. H. RICHARDSON

Fertilizing value of activated sludge (BROWN) 14. Colloidal phosphates (ELSCHNER) 8.

Fertilizer. J. H. HUFFSTUTTER. U. S. 1,438,830, Dec. 12. Sawdust in porous bags is immersed in a satd. soln. contg. decomposed animal and vegetable matter such as is obtained from stable manure and the contents of the bags are afterward drained and dried.

Fertilizer. A. L. KREISS. Can. 226,546, Nov. 28, 1922. Phosphate rock is fed into a heated drier contg. a soln. of an alkali metal salt and the mixt is dried. Cf. C. A. 16, 2184; 17, 323.

Fertilizer. J. GORBING. Can. 226,610, Nov. 28, 1922. A fertilizer is produced by reacting on waste lye from cellulose manuf. with quick lime and MgO.

Fertilizer. L. D. POOCK. U. S. 1,439,188, Dec. 19. A liquid fertilizer is formed of an infusion of deciduous leaves, together with sol. yeast-fermentation products of the leaves, prepd. by permitting a 10-20 day fermentation with bakers' yeast.

Fertilizer from tankage. J. P. HAMLER. U. S. 1,437,973, Dec. 5. Tankage is digested with SO₂, freed from a large amt. of H₂O by expression, and the expressed liquor is concd. and returned to the material from which it was sepd. and the mixt. is then dried.

Phosphatic fertilizer. E. C. SOPER. U. S. 1,437,456, Dec. 5. Phosphate rock is mixed with NaHSO₄ 22 1/4% and ground corn cobs or sawdust 7 1/4% and with such a limited amt. of H₂O as to leave the mixt. in pulverulent condition and it is then calcined at a temp. of about 1320-1430° to form a fertilizer.

Curing acid phosphate. E. H. ARMSTRONG. U. S. 1,439,054, Dec. 19. Acid phosphate is cured by treatment with a rising current of air in vertical towers or chambers through which the acid phosphate descends, followed by similar treatment with unheated air. The mass is subjected to centrifugal action during its downward movements.

Soluble lime-sulfur composition. E. H. FRENCH, J. R. WITHROW AND A. O. ALLEN. U. S. 1,437,838, Dec. 5. A compn. adapted for use as an insecticide and fungicide is prepd. by mixing Ca(OH)₂ 1 and S 2 parts with H₂O and heating to form a 32-35° B \acute{e} . soln. which is filtered and then mixed with 5% of glue or tankage and evapd. *in vacuo*.

Insectifuge paint. C. F. ARMITAGE, B. C. BERRY AND F. H. HOLMES. U. S. 1,439,053, Dec. 19. Oil of cedar leaf 1, oil of cedar wood 9, paraffin 1 and coloring matter 0.5 part.

16—THE FERMENTATION INDUSTRIES

C. N. FREY

Production of acetone, alcohol, and acids from oat and peanut hulls. E. B. FRED, W. H. PETERSON AND J. A. ANDERSON. *Ind. Eng. Chem.* 15, 126(1923).—Acetone, alc., and acids may be produced from hydrolyzed oat hulls, peanut hulls, and corn cobs. The hulls are hydrolyzed with 2% H₂SO₄ for 2 hrs. at 15 lbs., and the soln. is then neutralized with CaCO₃. Oat hulls yield 26.5% reducing sugar, and peanut hulls 7.6%. Peptone and Na phosphate were added to the diluted sirup, and the solns. inoculated with *B. acetotyllicum*. The reducing sugars of both materials are completely fermented, oat hulls yielding, on the basis of 100 lbs., 3.9 lbs. acetone, 7.2 lbs. C₂H₅OH, and 1.4 lbs. volatile acids. Peanut hulls give a much lower yield. *Lactobacillus pen-tacehicus* did not completely ferment the sugar. C. N. F.

Lactic fermentation. Action of very small portions of apparently inactive substances. CHARLES RICHET AND A. G. LEBER. *Compt. rend.* 175, 1021-4(1922).—Forty tubes each contg. exactly the same quantity of bouillon culture were divided in 2 series, 20 contg. the substance to be tested and 20 to serve as controls. To each of the 40 tubes are added equal amts. of phenolphthalein and all sterilized. The contents of the tubes are then inoculated by aid of the Pt loop and subjected to fermentation under identical conditions. The degree of fermentation is measured by the amt. of KOH necessary to produce a rose tint in the culture. Tests were made with urea and with milk, the results showing that these apparently inactive substances, even in ex-

treme diln. (0.001 to 0.00001 g. per l.), have a decided effect on the production of lactic acid, the figures varying from 70 to 134 compared with controls at 100. In general stronger concns. of urea or milk retard the production of lactic acid and weaker concns. accelerate it.

L. W. RIGGS

The causation of "ropiness" in worts and beers. P. HAMPSHIRE. *Bull. Bur. Bio-Tech.* 1922, 199-214; cf. *C. A.* 17, 178.—The cells of *Acetobacter R* and similar species form considerable amts. of mucilaginous material, which swells and partially passes into soln. in the beer, causing ropiness. Ropiness decreases rapidly with increasing acidity. Acidity is increased by exposure of the beer surface to air, producing turbidity and film, but decreasing ropiness. The mucilaginous matter was pptd. with acetone or alc., dried and examd. It swells in water and on shaking passes into colloidal soln. It gives practically no protein reactions and appears to be of the nature of a dextran. *Acetobacter R* only produces ropiness in presence of beer or wort, glucose being necessary for its formation in bitter beer. Hops have no effect on the production of ropiness. *Acetobacter R* does not produce ropiness in milk. The presence of different species of acid-forming bacteria such as varieties of *Lactobacillus* and yeasts does not prevent the formation of ropiness by *Acetobacter R*.

F. L. SRYMOUR-JONES

New practices in the treatment of wines, particularly fruit wines. VON DER HEIDE. *Mitt. deut. Landw.-ges.* 37, 687-92 (1922).—A general discussion, with particular reference to the use of pure yeast cultures and SO₂; the formation, artificial reduction and propagation of acids; filtering and clarifying; and the addition of H₂O and sugar in making fruit wines.

K. D. JACOB

Casse, wine defects not directly caused by microorganisms. P. DECASTELLA. *J. Dept. Agr. Victoria* 20, 418, 431-81, 490-615, 621-73, 679 (1922).—A review together with a discussion of the maturation of wine.

RUSSELL M. JONES

Effect of salts upon the acid hydrolysis of wood. E. C. SHERRARD AND W. H. GAUCER. *Ind. Eng. Chem.* 15, 63-5 (1923).—Attempts were made to find catalysts that would increase the yield of EtOH formed on fermentation following acid hydrolysis of wood (white spruce sawdust). Results of about 70 expts. are reported. No definite conclusions are drawn, but in general the salts of metals of any one group in the periodic table behave similarly. Somewhat increased yields were obtained with 2-hydroxynaphthalene-6-sulfonic acid, which indicate possibilities in the field of hydrolytic catalysts.

L. E. WISE

Sulfite alcohol (DU BOIS-ESSELIN) 23.

Acetone and butyl alcohol by fermentation. C. WEIZMANN. U. S. 1,437,697, Dec. 5. This pat. relates to a modification or improvement upon the process of U. S. pat. 1,315,585 (*C. A.* 13, 2882). Chestnuts or similar nutty substances rich in starch are used for prep. a mash by heating with steam at 120-130° under pressure. Malt, 5-6%, is added to the mash, at 60-70°, and this serves to thin the mash sufficiently that frothing does not cause trouble during fermentation. The dild. mash is then inoculated and fermented to obtain acetone and Bu alc. in a 72 hr. fermentation.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Camphor. F. SCHMITT. *Caoutchouc & gutta-percha* 19, 11649(1922).—Chiefly a description of the Japanese camphor industry, and the properties and uses of camphor. Tests were made of the relative volatility of 3 grades of natural camphor: (1) refined pharmaceutical grade, (2) camphor BB, the unrefined compressed wood distillate contg. 95–7% camphor and 0.04–.05% EtOH-insol. and (3) camphor B, the crude wood distillate of 92–5% purity. After 24 hrs. *in vacuo* (12 mm.) the following % losses in wt., resp., were found: 39.18, 51.78, 46.53. C. C. DAVIS

Experiments on the distillation of camphor leaves from Tonkin. G. VERNET. *Caoutchouc & gutta-percha* 19, 11650–3(1922).—Twenty samples of varying quality were distd. by means of a Chamberland autoclave with a Bussy condenser with repeated distn. and condensation at -5° of the liquid to recover all camphor. The results in % camphor were: Ban Gia, 0, 0.40, 0; Ban Thinh, 0.358; Yen Khoai, 0.599, 1.605; Rinh Chua 0, 0; Na Gia, 0, 0; Phuong Lan, 0, 0, 0, 0.087, 0, 0; Dai Giap, 1.24, 1.60, 0.26. A comparison of these data was made with those obtained by previous observers (references given). Only the 2nd Yen Khoai and the 2nd Dai Giap samples gave yields approaching those from the Italian leaves, and it is considered that these are the only 2 varieties worthy of cultivation. C. C. DAVIS

Estimation of morphine. J. R. NICHOLLS. *Analyst* 47, 506–10(1922).—Expts. to det. the most favorable conditions for the rapid and complete extn. of morphine show that, when 2 vols. of ammoniacal 50% EtOH soln. of morphine are shaken with 1 vol. of CHCl_3 , about 85% of the total alkaloid passes into the lower layer. By making the ratio of H_2O , EtOH and CHCl_3 approx. the same in each extn., all the morphine can be removed in 3 or 4 extns. The alkaloid in the ext. is estd. either by titration, colorimetrically or polarimetrically. W. O. E.

Adulterant of licorice paste. A. H. BENNETT. *Analyst* 47, 511(1922).—A form of adulteration quite frequently practiced in recent years consists in the addn. of ext. of *Carlina gummifera* known in the Sicilian dialect as *Masticogna*. An ext. of this sort yields on hydrolysis up to 60% reducing sugars, the normal paste being generally from 8 to 12. Admixt. with masticogna ext., therefore, gives a product unduly high in sugar, while the starch and glycyrrhizin will be notably diminished. While similar effects are produced by other vegetable exts., the presence of even moderate amts. of masticogna can be recognized by the microscopical examn. of the insol. residue through crystals of Ca oxalate of very small dimension and characteristic form. A photomicrograph of such a residue is shown. W. O. E.

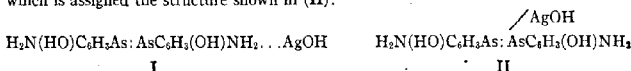
Essential oils from *Leptospermum liversidgei*. A. R. PENFOLD. *J. Proc. Roy. Soc. N. S. Wales* 56, 82–5(1922); cf. *Ibid* 39, 124(1905).—P. concludes that in all probability there are at least 2 distinct forms, if not 3, of this shrub, one yielding an oil to the extent of 0.25 to 0.30%, as originally described by Baker and Smith (*l. c.*), contg. about 35 to 50% citral (no citronellal); a form yielding about 0.55% oil contg. 70 to 80% citronellal (no citral); and a form yielding about 0.6 to 0.8% citral (no citronellal?). The phys. consts. obtained are given. W. O. E.

Variation statistic as auxiliary science of pharmacognosy. VIII. L. ROSENTHALER. *Ber. pharm. Ges.* 32, 237–45(1922); cf. *C. A.* 15, 919; 16, 1483.—Oil content of sweet and bitter almonds. In the case of sweet almonds. the oil content varied from 45.3 to 87.1% (exclusive of 21.5% found for one of the 20 samples examd.), the smaller seeds yielding as a rule the most oil. Almost 73% of the 23 samples of bitter almonds examd. possessed an oil content varying between 45 and 55% (highest 65, lowest 35%). In

the case of bitter almonds the oil content of the larger nuts was greater than that of the smaller nuts. *Amygdalin content of apricot and peach kernels.* The amt. of amygdalin present was detd. indirectly by means of the HCN developed. In the case of both apricot and peach kernels, the smaller samples show a somewhat higher amygdalin content.

W. O. E.

Isomeric silver arspenamines. A. BINZ AND W. H. LUDWIG. *Ber.* 55, 3826–31 (1922).—The light brown substance arising from the union of arspenamine and AgNO_3 , and subsequent pptn. with Na_2CO_3 is stable toward H_3PO_4 and assumed to possess the structure shown in (I). On soln. of this product in aq. NaOH and pptn. with CO_2 , there results a deep brown substance sol. in Na_2CO_3 and unstable toward H_3PO_4 , to which is assigned the structure shown in (II):



Expts. are fully described leading to the isolation of these 2 isomers. Both (I) and (II) are purely hypothetical and arbitrarily assigned.

W. O. E.

Localization of hydrocyanic acid glucosides and emulsin in bitter almonds and cherry laurel leaves. L. ROSENTHALER AND K. SEILER. *Ber. pharm. Ges.* 32, 245–8 (1922).—There being no serviceable microchem. tests available for the direct identification of amygdalin and prulaurasin, recourse is had to the detn. of their scission products, notably HCN. To this end the authors have studied the reactions obtained with emulsin on these glucosides in the presence of iodized rice starch grains under the microscope. The technic followed is fully outlined and the results obtained show the localization in detail.

W. O. E.

Congelation of essential oils. W. J. SANDERSON AND W. J. JONES. *Chemistry & Industry* 42, 1–2T(1923).—Several essential oils on being cooled slightly below room temp. deposit crystals of their chief constituent, as anethole from aniseed, sweet fennel and star-aniseed oils, safrole from sassafras and the higher camphor oils, and Me *n*-nonyl ketone from rue oil. While this behavior has been recognized as a good test of the quality of these oils, no systematic investigation of the subject has hitherto been undertaken. In the present study particular attention was paid both to thermometry and the purity of the substances employed. Tests were carried out with the purified oils, and with binary control mixts. made up in known proportions by wt. The authors show that the results obtained in 3 series of expts. involving anethole, Me *n*-nonyl ketone and safrole solns. of various solutes may be used as a basis for ascertaining how much of the main constituent a given sample of a congealing oil contains.

W. O. E.

Composition of cacao butter. C. T. KINGZETT. *Chem. Trade J.* 71, 699(1922).—In an earlier study (cf. *J. Chem. Soc.* 33, 38(1878)) K. reported the presence among the acid constituents of cacao butter of 2 acids believed to have the formulas $\text{C}_{13}\text{H}_{22}\text{O}_2$ (lauric acid), and $\text{C}_{16}\text{H}_{30}\text{O}_2$ to which latter was assigned the name "theobromic acid." While subsequent investigators have been unable to substantiate K's. findings with respect to these acids, the study was taken up anew in a limited way, especially in answer to the question as to whether there is a theobromic acid. While the results now reported are mostly negative, in that the presence of "theobromic acid" could not be verified, a product approaching the compn. of lauric acid was isolated, thus seemingly confirming the result in part of the earlier investigation. The need for a more comprehensive study of cacao butter is emphasized.

W. O. E.

Miscibility test for eucalyptus oils. C. E. FAWSITT AND C. H. FISCHER. *J. Proc. Roy. Soc. N. S. Wales* 56, 109–114(1922).—In the method described the oil is

mixed in definite proportions with a suitable liquid, say an aq. alc., giving 2 layers of liquid at the ordinary temp. The crit. soln. temp. is then detd. by heating until only 1 layer is formed, and then allowing to cool until a cloudiness develops. This value (C.S.T.) has been found to alter considerably with slight changes in the compn. of the oil, and so this method of testing the miscibility gives a more sensitive way for detg. the vol. of aq. alc. required for complete soln. of 1 vol. of the oil involved. To eliminate the effect due to varying proportions of H_2O in the sample, the oil should either be dried before testing or else satd. with H_2O . The authors employed the latter course. The change in C.S.T. observed in varying periods of heating after mixing must correspond to some mol. change in the soln., probably due either to reaction between the cineole and the alc. (MeOH in the series of expts. described), or to condensation of the aldehyde present in the oil. In the authors' expts. 1 cc. of the oil was mixed with 1 cc. of the alc.- H_2O mixt. in a small tube about 1 cm. in bore and 5-8 cm. long, the open end being drawn out somewhat and fitted with a cap consisting of a piece of rubber tube and a piece of glass tube drawn out to a very small opening. This app. was then bound tightly by rubber bands to a thermometer, the liquid contents of the tube being exactly opposite the bulb. The whole was then immersed in a large beaker contg. H_2O , the temp. being raised until the 2 layers of liquid completely mixed, and the C.S.T. then noted. Among other phenomena observed in several series of expts. was the fact that a change in the compn. of the mixt. by 1% pinene produces a difference in the C.S.T. of 1 to 2°.

W. O. E.

Australian Melaleucas and their essential oils. VI. R. T. BAKER AND H. G. SMITH. *J. Proc. Roy. Soc. N. S. Wales* 56, 115-24(1922).—Summarizing the results obtained for the oil of *M. ericifolia* it may be stated that it differs from that of "cajuput" in the following particulars: the d. is much lower; the terpenes are strongly dextrorotatory; it contains besides *d*-terpineol considerably less cineole, the chief oxygenated constituent being terpineol and not cineole. The following consts. for the crude oil, obtained in a 0.84% yield from fresh leaves and terminal branchlets, were detd.: d_{15}^4 0.8938, α_D^{20} 13.3°, n_D^{20} 1.4705. For the crude oil distd. from young material of *M. Deanei* F. v. M. and obtained in a yield of 0.7% consts. were detd. as follows: d_{15}^4 0.8888, α_D^{20} 22.7°, n_D^{20} 1.4646, sapon. no. for esters 5.7 = 2% terpinyl acetate (after acetylation 18.6 = 4% free terpineol).

W. O. E.

Essential oil of *Backhousia myrtifolia*. A. R. PENFOLD. *J. Proc. Roy. Soc. N. S. Wales* 56, 125-9(1922).—The oil obtained by steam distn. in a 0.42% yield from the leaves and terminal branchlets is apparently subject to seasonal variations, but contains as the chief constituent elemicin, a somewhat rarely occurring phenol ether, present to the extent of 75 to 80%, the remainder being pinene, a paraffin, sesquiterpene, unidentified alcoholic and phenolic substances.

W. O. E.

Occurrence of *l*-phellandrene in the oil of *Melaleuca acuminata*. H. G. SMITH. *J. Proc. Roy. Soc. N. S. Wales* 56, 159-61(1922).—The crude oil obtained in a 1.7 to 2 % yield was almost colorless, very mobile, and contained considerable cineole (about 43.7%), had d_{15}^4 0.8985, α_D^{20} -12.8°, n_D^{20} 1.4690, acid no. 1.1, sapon. no. 4.5, sapon. no. of esterized oil 21.2. The principal terpene consisted of *l*-phellandrene (nitrosite m. 105-6°), apparently not identical in constitution with the *l*-phellandrene occurring in the oils of species belonging to the "peppermint group" of Eucalypts.

W. O. E.

Essential oils of two *Leptospermums*. A. R. PENFOLD. *J. Proc. Roy. Soc. N. S. Wales* 56, 162-9(1922).—The crude oils, obtained from the distn. of 2 lots of leaves and terminal branchlets of *L. flavescens* var. *microphyllum*, had as the principal constituents *d*, α -pinene, sesquiterpenes (probably eudesmene as the chief one), unidentified sesquiterpene alc. and cineole (3 to 5%). The oil obtained in a 1.13% yield from the leaves and branchlets of *L. flavescens* Sm. var. *leptophyllum* Cheel was a pale yellow

mobile liquid having the following characters: d_{20}^4 0.8990, optical rotation 14.12° , n_D^{20} 1.4810, soly. in 80% EtOH 1 in 7 by wt., ester no. hot 1.5 hrs. 2.04 (do. after acetylation 1.5 hrs. 63.24). The principal constituents are α - and β -pinene, cineole, α -terpinol, sesquiterpene and sesquiterpene alc. W. O. E.

Necessity for more stringent tests of German pharmacopoeial preparations containing sugar and alcohol. O. SCHMATOLLA. *Pharm. Zentralhalle* 63, 609-11 (1922).—A discussion of the prevailing after-war conditions, under which a more exact control of spirituous and saccharine pharmacopoeial products appears necessary, more particularly of a procedure for the evaluation of *Tinct. Ferri aromatica*. W. O. E.

Talc specifications. C. L. SPEIDEN. *Ungerer's Bull.* 3, 9-10 (1922).—It is shown that talc should contain the lowest possible quantity of acid-sol. matter, be absolutely white, possess the extremely valuable quality of "slip" to a high degree coupled with adhesiveness, have moderate luster and avoid "shine." W. O. E.

An arsenical glucoside—diglucosidodihydroxydiaminoarsenobenzene. A. AUBRY AND E. DORMOV. *Compt. rend.* 175, 819-22 (1922).—Arsphenamine reacted with glucose to form diglucosidodihydroxydiaminoarsenobenzene, $[\alpha]_D = -560^\circ$; it seemed probable that the glucose was attached to the amino group of the arsenphenamine. Hydrolysis took place slowly in pure water, but was hastened by the addition of acid; the addition of glucose retarded the hydrolysis. For therapeutic uses the glucoside seemed to possess certain advantages over arsenphenamine. DONALD W. MACARDLE

Problems, we, as officials, have in common with the trade. ARNO VIEHÖVER. *J. Am. Pharm. Assoc.* 11, 592-5 (1922).—Discussion of the methods of drying, cleaning and storing of drugs. L. E. WARREN

The approximate densities of ammoniated mercury and zinc oxide.* J. A. W. LUCK. *J. Am. Pharm. Assoc.* 11, 596-9 (1922).—Formulas are given by which it is possible to calc. the ds. of most ointments. The calcd. values for several ointments are given: boric acid 0.86, ammoniated Hg 0.90, yellow HgO 0.97, dild. Hg 1.12, Hg 1.76, I 1.03, CHI₃ 1.01, C₆H₅OH 0.94, simple ointment 0.93, rose water 0.94, S 1.00, ZnO 1.23, belladonna 0.95, stramonium 0.95, galls 0.93, tannic acid 0.95, chrysarobin 0.93, and tar 0.99. L. E. WARREN

Diethylphthalate. J. A. HANDY AND L. F. HOYT. *J. Am. Pharm. Assoc.* 11, 928-39 (1922).—For a number of years this compd. has been used as a fixative in perfumery. Recently it has attracted much attention as a denaturant of EtOH for use in perfumery. H. and H. have examd. 8 com. specimens with the following results: $d_{15.4}^{20}$ 1.1218-1.1261; n_D^{20} 1.5008-1.5020; $[\alpha]_D^{20} -0^\circ$, 26.4 to $+0^\circ$, 6.2; free acidity as phthalic acid 0.017-0.105%; sapon. no. 500.82 to 504.16; 99.16 to 99.82% ester; sapon. no. corrected for free acidity 500.49 to 503.99; 99.09-99.78% ester; $b_{73.4}$ 295° , b_{30} 182° , b_{14} 163° ; surface tension, static, dynes per cm. 25° 42.5; flash p. (sample 2) 153.3° . Of the esters of phthalic acid the diethyl ester has been found the most satisfactory as a denaturant and fixative in perfumery. It is the most stable, has the greatest freedom from color and odor and gives the most uniform evapn. and lasting quality to odors. L. E. W.

A rapid assay method for the determination of ascaridole in oil of chenopodium. E. K. NELSON. *J. Am. Pharm. Assoc.* 10, 836-7 (1921).—Agitate 10 cc. of the oil with 60% HC₂H₃O₃ in a Cassia flask, fill to the mark with the solvent and allow to stand. Subtract the vol. of undissolved oil from the original vol. and multiply the remainder by 10. Five specimens ranged from 48 to 73% of ascaridole. L. E. WARREN

BAUER, H.: *Analytische Chemie der Alkaloide*. Berlin: Gebrüder Borntraeger. 425 pp. 30s.

LLOYD, JOHN URI: *Origin and History of All the Pharmacopoeial Vegetable Drugs*,

Chemicals and Preparations, with Bibliography. Vol. I. Vegetable Drugs. Washington, D. C.: American Drug Manufacturers' Association. 356 pp. Reviewed in *Am. J. Pharm.* **94**, 759(1922).

PARRY, R. J. **The Chemistry of Essential Oils and Artificial Perfumes.** 2 Vols. London: Scott, Greenwood & Son. Vol. I, 549 pp. 30s. Vol. II, 364 pp. 21s.

Silver derivative of aminomercaptobenzoic acid. A. FELDT. U. S. 1,439,624, Dec. 19. 2, 4-AgS(H₂N)C₆H₃COOH is obtained by reaction of a Ag salt such as AgNO₃ upon 2, 4-HS(H₂N)C₆H₃CO₂H. It is a colorless powder, difficultly sol. in H₂O, readily sol. in dil. acids and alkalis and m. 205°. Its alkali metal salts are proposed for use as bactericidal therapeutics.

Dihydroisoquinoline derivatives. M. HARTMANN and H. KAGI. U. S. 1,437,802, Dec. 5. Methyl β-(3,4-dimethoxyphenyl)-α-(benzoylamino) propionate, fine needles, m. 104-5°, obtained by hydrogenation of Me veratralhippurate in MeOH soln., is condensed at 130-5° with P oxychloride to form methyl 1-phenyl-6,7-dimethoxy-3, 4-dihydroisoquinoline-3-carboxylate, m. 122.5° after recrystn. from MeOH. Its hydrochloride and hydrobromide form yellow crystals easily sol. in H₂O. MeI reacts with the free ester to form a *N*-methiodide, difficultly sol. in H₂O, which is converted by AgCl into an easily sol. methochloride. Hydrogenation of methyl piperonalhippurate produces α-benzoylamino-β-piperonylpropionate, brilliant needles, m. 126-7°; this on condensation yields methyl 1-phenyl-6,7-methylenedioxy-3,4-dihydroisoquinoline-3-carboxylate, colorless needles, m. 140.5°. Methyl-α-piperonylamino-β-piperonyl propionate, glassy needles m. 139-40°, yields on condensation methyl 1-3',4'-methylenediphenyl-6,7-methylenedioxy-3,4-dihydroisoquinoline-3-carboxylate, m. 140-1; the hydrochloride is partly decomposed by H₂O. Methyl 1-phenethyl-6,7-methylenedioxy-3, 4-dihydroisoquinoline-3-carboxylate, prisms, m. 111°, is obtained by condensation of methyl α-(β-phenylpropionylamino)-β-piperonylpropionate, m. 127°, formed by the hydrogenation of methyl α-cinnamylamino-β-3,4-methylenedioxyphenylacrylate m. 192°. This compd. is prepd. by heating equimol. proportions of piperonal, cinnamylglycocol and NaOAc and 3 mol. proportions of Ac₂O and boiling the product with MeOH and soda. The 6,7-dihydroxy derivs. have therapeutic properties similar to those of hydrastinine but are less toxic than the latter or its synthetically prepd. derivs.

Spleen extract. R. A. ARCHIBALD. U. S. 1,437,951, Dec. 5. A sol. ext., which when injected parenterally stimulates production of an increased number and activity of red blood cells and hemoglobin and activity of leucocytes and blood platelets, is prepd. by forming an emulsion of a spleen with a small amt. of PhOH, heating to destroy antiferments, autolyzing, pptg. proteins with HOAc, filtering, adding more PhOH, neutralizing with NaOH and filtering.

Crystallizing caffeine. T. SCHULZE. U. S. 1,438,558, Dec. 12. A soln. of caffeine is dehydrated to a considerable extent by heating in a vat and the residue of the soln. is heated as a layer upon a cheese cloth drying belt to a temp. above that employed in the partial dehydration, in order to obtain pure crysld. caffeine.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Developments in heavy acids and alkalies. P. PARRISH. *Chem. Age* (London) **7**, 921-3(1922).—A review. E. J. C.

Hand-rubber lined steel tanks for transporting hydrochloric acid. F. C. ZEISBERG.

Ind. Eng. Chem. **15**, 157-8(1923).—Experience with one exptl. tank is described.

F. C. Z.

Potash from kelp. VII. **The manufacture of potash salts.** J. W. TURRENTINE, H. G. TANNER AND P. S. SHOAF. *Ind. Eng. Chem.* **15**, 159-63(1923).—The process used at the exptl. plant of the Bur. of Soils at Summerland, Cal. is described. F. C. Z.

The utilization of potassium in potash feldspar. F. JOHNSON. *Norges Geol. Undersøkelse* **109**, 77 pp.(1922). (Publication No. 9 of Norwegian Governmental Raw Materials Committee.)—An extensive review is given of patent and journal literature on the extn. of K from feldspar. With present prices of K, the only method now economically possible in Norway is the utilization of dust from cement kilns, which would yield 700 tons K_2O annually out of a total consumption of 5,000 tons. Feldspar seldom occurs as a pure mineral in large masses and no effective method of concn. is known. High-grade feldspar is valuable as such and commands a price higher than that of its K content. The proposed chem. processes are all too costly. S. G.

Production of caustic calcined magnesite in the Scott furnace. W. C. RIDDELL AND C. N. SCHUETTE. *Eng. Mining J.-Press* **114**, 981-4(1922).—The Scott furnace was invented and first used at a quicksilver mine in California in 1875. There are no movable parts. The ore is charged from the top into shafts fitted with staggered tile shelves inclined at 45° and so placed that the space between the successive shelves is from 4 to 6 in. according to the depth of ore bed desired. The hot gases pass horizontally along these shelves. The furnace is discharged through doors in the side walls. Oil, atomized with steam, is used as a fuel. For producing caustic calcined magnesite a temp. range from 880° at the firebox to 580° , where the gases pass into the stack after 3 passes along the shelves of ore, is maintained. This is considerably higher than the temp. for treating Hg. The furnace can be operated entirely by unskilled labor. Draft, temp., and rate of feeding can be closely and easily controlled within desired limits and fuel efficiency is high. Every part of the furnace is accessible to proper tools and inspection. Details of construction and operation are given.

F. W. COBB

The extraction of glucina (beryllia) from beryl. H. T. S. BRITTON. *J. Soc. Chem. Ind.* **41**, 349-52T(1922).—Beryl can be safely fused in a Ni crucible if the temp. is kept low. Fusion with potash is most convenient. B. investigated the slight soly. of alum, and found that the best conditions are obtained by adjusting the concn. of H_2SO_4 in the mother liquor to about 5 N by the addn. of KOH, and then satg. the boiling soln. with K_2SO_4 and crystg. preferably at 0° . About 92% of the Al_2O_3 is thereby sepd. in 1 step. The beryllia can be extd. with cold concd. NaOH sufficient to redissolve the ppt., dilg. and boiling for 40 min.

G. R. FONDA

Manganese dioxide produced by chemical process in California. GEO. J. YOUNG. *Eng. Mining J.-Press* **114**, 980(1922).—The ore, contg. MnO_2 , is ground and digested with H_2SO_4 . The clear filtrate is treated with $Ca(NO_3)_2$ from Norway and $Mn(NO_3)_2$ is obtained, $CaSO_4$ being pptd. The soln. is evapd., filtered, and evapd. under vacuum. The $Mn(NO_3)_2$ is heated in retorts and associated into MnO_2 and HNO_3 , the acid being recovered by a series of scrubbing towers. The HNO_3 in the first tower has a sp. gr. of 1.38 and is almost chemically pure. A high grade of MnO_2 is obtained.

F. W. COBB

The manufacture of calcium citrate and citric acid (from limes). ANON. *Tropical Agr.* **53**, 22-8(1922).—A general discussion.

M. S. ANDERSON

Lime in 1921. G. F. LOUGHLIN AND A. T. COONS. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. II, 155-68(preprint No. 25, publ. Nov. 29, 1922).

E. J. C.

The significance of the German potash industry. BADERMANN. *Chem.-Ztg.* 46, 1122-4(1922). E. H.

The marketing of salt. W. C. PHALEN. *Eng. Mining J.-Press* 115, 185-90 (1923).—Besides a consideration of marketing a discussion is included of uses, occurrence, consumption, grades and purity, with some analyses. E. J. C.

Salt, bromine and calcium chloride in 1921. K. W. COTTELL. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. II, 117-23(preprint No. 20, publ. Aug. 31, 1922). E. J. C.

Arsenic, bismuth, selenium and tellurium in 1921. V. C. HEIKES. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. I, 129-42(preprint No. 14, 1922). E. J. C.

Barites and barium products in 1921. G. W. STOSE. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. II, 125-34(preprint No. 21, publ. Sept. 11, 1922). E. J. C.

The nitrogen industry in 1922. E. B. MAXTED. *Chem. Age* (London) 7, 917-9 (1922). E. J. C.

Economic status of nitrogen fixation in Germany. W. T. DAUGHERTY. *Chem. Met. Eng.* 28, 62-4(1922). E. J. C.

The world's trade in sulfur. ANON. *Chem. Trade J.* 71, 761-3(1922). E. J. C.

Asbestos in 1921. EDW. SAMPSON. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. II, 135-42(preprint No. 22, publ. Sept. 19, 1922). E. J. C.

Transformation of gypsum into ammonium sulfate. C. MATIGNON AND M. FREJACQUES. *Compt. rend.* 175, 33-5(1922).—The manuf. of $(\text{NH}_4)_2\text{SO}_4$ by the double decompn. of CaSO_4 and $(\text{NH}_4)_2\text{CO}_3$ is of importance owing to the high price of pyrites, necessity of saving H_2SO_4 , and the rapid development of the synthetic NH_3 process. With com. gypsum (94.06% pure) and concd. solns. of $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{SO}_4$ in varying amts. the equil. was practically reached after 5 hrs. agitation and the coeff. of transformation was over 96%. The velocity of the reaction was studied at 16° as a function of the concn. of the $(\text{NH}_4)_2\text{CO}_3$ solns., of the size of CaSO_4 grains and of the rate of stirring. The plotted data show the existence of 2 distinct phases, the first proceeding less rapidly than the second; this phenomenon has not yet been satisfactorily explained. In the first phase the velocity is greater the finer the size of the CaSO_4 . The faster the agitation the greater is the speed of the reaction. The presence of $(\text{NH}_4)_2\text{SO}_4$ in the initial soln. retards the completion of the reaction. The diln. of the $(\text{NH}_4)_2\text{CO}_3$ retards the transformation. Equil. is reached after $2\frac{1}{2}$ hrs. stirring. A slight excess (4-5%) of gypsum was used throughout. ACHILLE R. ALBOUZE

Bavarian graphite. EUGEN RISHKEVICH. *Chem.-Ztg.* 46, 1013-6, 1035-6(1922).—The graphite occurs in gneiss, replacing mica and associated with pyrite. It varies from 12 to 40%, usually 20 to 25%, C content, that under 12% not being worth mining. The ore comes in lenses, and mining is expensive. Crushing, sizing and wet concn., followed by fine grinding and concn., give a concentrate of 65% C, which can be raised to 80-90% by dewatering. Tests are described indicating the superiority of Bavarian graphite in elec. cond., heat cond., resistance to combustion, etc., when compared with other kinds. W. C. EBAUGH

United States Government specifications for fire-extinguishing liquid (carbon tetrachloride base). Federal Specification Board, *Standard Spec.* No. 36; *Circ. of Bur. of Standards* No. 134, 4 pp.(1922). E. J. C.

The deterioration of chloride of lime. L. GIZOLME. *Ann. fals.* 15, 148-9(1922).—Three lots of bleaching powder kept in wooden casks in a covered shed showed an

available Cl content of 24.2 and 12.0%, 21.4 and 14.6%, and 34.0 and 28.8% at intervals of 266, 211, and 190 days, resp., equiv. to a loss of 0.046, 0.034, and 0.027% per day, resp. Two months later the second and third lots tested 12.2% and 27.4%, showing further loss of 0.040 and 0.023% per day, resp.

A. P.-C.

The significance of mica minerals as a source of K for plants (GOLDSCHMIDT, JOHNSON) 15. Manufacture of carbon blacks in France (OSWALD) 30. Colloidal phosphates (ELSCHNER) 8.

Metallic and non-metallic chlorides. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE-Ges. Brit. 176,811, March 13, 1922. Inorg. chlorides are obtained by passing chlorine contg. S_2Cl_2 over a heated mixt. of an oxide and C; the production of $SiCl_4$ and $AlCl_3$ is particularly described. When $AlCl_3$ is prepd., the first product is a sublimate contg. an addition product of S_2Cl_2 with $AlCl_3$ from which the two chlorides are sepd. by distn., preferably under reduced pressure. The mixt. of Cl and S_2Cl_2 may be made by passing Cl through an evaporator containing S_2Cl_2 . Alternatively, the S_2Cl_2 may be formed *in situ*, e. g., by adding S compds. such as pyrites or a sulfate to the mixt. of C and oxide.

Contact sulfuric acid. H. F. MERRIAM. Can. 225,951, Nov. 14, 1922. S in the form of Louisiana brimstone is burned to produce SO_2 and O which are conducted over catalytic material to give a 97–98% conversion; the SO_3 formed is absorbed and the whole operation is conducted without permitting the temp. to fall materially below that required for the production of SO_3 in the converters.

Metallopyrophosphoric acids or their salts. B. LEVIN. Can. 226,670, Nov. 28, 1922. Metallic pyrophosphoric acids and their salts are combined with H_3BO_3 or B compds. to produce products which are less hygroscopic and less liable to revert to metallic phosphates than is the corresponding metal pyrophosphate. E. g., chrome alum is heated with H_3BO_3 and H_2PO_4 until the mass is anhyd. Such products are suitable for use in *tanning*.

Catalytic oxidation of ammonia. I. W. CEDERBERG and H. M. BÄCKSTRÖM. Brit. 181,486, March 15, 1921. The oxidation of NH_3 by means of O is effected by passing the gas mixt. through a catalytic zone in which the concn. of the catalyst gradually increases in the direction of the gas-flow; in this way mixts. contg. up to 40% of NH_3 can be treated without explosion. A suitable app. is specified.

Synthesis of ammonia. J. C. CLANCY. U. S. 1,439,291, Dec. 19. NH_3 is synthesized by the action of a catalyst prepd. by heating Ca ferrocyanide or other double CN compd. to about 400° or somewhat higher in contact with NH_3 . U. S. 1,439,292 relates to the prepn. of a catalyst in this manner for NH_3 synthesis. Catalysts thus formed are active at 325°. Cf. C. A. 16, 1134, 2013 and following pat.

Ammonia synthesis and catalyst. J. C. CLANCY. Can. 226,262, Nov. 21, 1922. A mixt. of $Ca_2Fe(CN)_6$ and $Ba_2Fe(CN)_6$ deposited on a porous support and activated by heating in an atm. of NH_3 is used for the synthesis of NH_3 . Cf. C. A. 16, 1134, 2013 and preceding pat.

Synthetic ammonia. L. CASALE. Can. 225,824, Nov. 14, 1922. A mixt. of H and N under high pressure is passed over a catalyst along with sufficient NH_3 to regulate the thermic effect of the reaction.

Alkali metal bromides. A. WEIDEL. U. S. 1,437,740, Dec. 5. NaBr or KBr is prepd. by the reaction of liquid Br on NaOH, Na_2CO_3 or KOH in the presence of $MnCO_3$,

Mn(OH)₂, or other manganous compd. decomposable by Br. MnO_2 is obtained as a by-product.

Stable solutions of alkali hypochlorites. R. MANDELBAUM. Ger. 330,192, Dec. 9, 1920. 500 parts of water glass of 38° Bé. are evapd. until 100-150 parts are lost. The soln. is cooled and partly stiffened and 10 parts NaOCl soln. of 35° Bé. are added; or a mixt. of 40 parts water glass of 38° Bé. and 2 parts NaOCl soln. of 35° Bé. is stirred up with 10 to 15 parts calcined soda. The resulting solns. are stable to light and air.

Solid calcium hypochlorite. CHEM. FAB. GRIESHEIM-ELEKTRON. Ger. 282,746, Mar. 19, 1915. This is an improvement upon patent 195,896. To a mixt. of 1 part CaO and 2 parts, at most, of H₂O is added the required amt. of Cl with stirring. The temp. is kept between 35-45° and the pressure about 500 mm. water column until near the end of the process when the temp. may be allowed to sink to 25° and the pressure to rise to 2000 mm. water column.

Chloride of lime. J. L. CARL ECKELT. Ger. 309,667, Dec. 6, 1918. The chamber in which CaO reacts with Cl gas is provided with shelves one above the other in such a way that scrapers manipulated from outside the chamber cause the charge of CaO which is filled in from the top upon the upper shelves to fall in succession upon the lower shelves during the course of the reaction. The Cl is introduced into the chamber from the bottom and is stirred up by the falling of the CaO from one shelf to the next. The freshly introduced CaO reacts most rapidly with the Cl and accordingly there is more heat developed in the upper portions of the chamber. To counteract this a cooling liquid is conducted through vertical pipes located along the walls, the fluid passing downward.

Chloride of lime. J. L. CARL ECKELT. Ger. 310,271, Jan. 6, 1919. The reaction chamber is provided with holes in the ends which may be tightly closed, and through which it is possible to enter the chamber to make repairs. The plates upon which the CaO is placed are supported by short projections from the walls and are easily replaceable.

Chloride of lime. J. L. CARL ECKELT. Ger. 311,219, March. 15, 1919. Upon the top of the reaction chamber is a series of filling shafts each divided by a horizontal slide into an upper and a lower portion. The lower portion of each filling shaft is sepd. from the reaction chamber by a similar slide. The corresponding slides of the filling shafts are connected with draw bars in such a way that all of the upper sections of the filling shafts can be emptied simultaneously into the lower sections, and the lower sections into the reaction chamber. In the reaction chamber are shelves arranged one above the other and the CaO falling upon the uppermost shelf is scraped off upon the shelf next below and so on in succession, falling eventually upon a series of rotatable valves which when closed form a floor for the reaction chamber. When the reaction is complete the valves are opened and the CaOCl₂ falls into the lowest chamber, from which it may be taken as desired.

Chloride of lime. E. SIDLER. Ger. 329,178, Nov. 16, 1920. The reaction chamber contains several plates arranged upon a single vertical shaft. Over each plate are stationary stirring scrapers which when the plates loaded with CaO are revolved by the shaft cause the CaO to travel first towards the center of the plates and then towards the circumference. In the walls of the chamber on alternate sides are passageways for the passage of the CaO from the plates above to those below.

Chloride of lime. A. PFÜLF. Ger. 329,844, Nov. 30, 1920. Within the chamber instead of shelves and scrapers are swinging or rotary members placed one above the other. These members may have various forms of cross-section.

Piezo-electric crystal. A. M. NICOLSON. U. S. 1,438,965, Dec. 19. Na K

tartrate crystals are prepd. with a face (one side of which is reëntrant) normal to a principal axis.

Extraction with solvents in a centrifugal apparatus. B. JUNQUERA. U. S. 1,438,809, Nov. 28. Extn. of Na or K chlorides or nitrates values from ores or other sol. substances is effected by retaining the comminuted solid material by centrifugal force against the perforated peripheral wall of a rotating receptacle while solvent liquid is passed through the material from the outside to the inside of the drum (to prevent solid particles being carried off by the centrifugal action).

Purifying soluble substances by froth flotation of insoluble impurities. W. BROADBRIDGE, E. EDGER and W. G. SELLERS. U. S. 1,439,061, Dec. 19. Crude caliche or other sol. substance contaminated with insol. impurities is dissolved and insol. matter is sepd. from the soln. by froth flotation.

Barium peroxide. A. J. JEWELL. U. S. 1,438,377, Dec. 12. Hydrated Ba(OH)₂ is sprayed into the top of a heated tower where it first undergoes evapn. to drive off H₂O of crystn. and is then converted into BaO₂ by the action of O.

Furnace adapted for producing iron oxides from sulfates. T. FRENCH. U. S. 1,438,372, Dec. 12.

Iodine. O. VON FABER. U. S. 1,438,071, Dec. 5. See Brit. 168,324 (C. A. 16, 319).

Hydrogen from reaction between steam and iron. E. B. MAXTED. U. S. 1,438,387, Dec. 12. Fe oxide is reduced by the action of CO and H₂ water gas or other reducing gas free from steam which contains less than 10% of N or a similar diluent, over 10% CO₂, and CO in substantially as great an amt. as the CO₂ and H₂. The reduced Fe is then treated with steam to form H.

Separating and compressing hydrogen. G. CLAUDE. U. S. 1,438,581, Dec. 12. A mixed gas contg. H and CO is compressed to 50–300 atm. and circulated at a temp. of –40° to –60° in contact with Et₂O or other solvent which in a single operation absorbs substantially all of the gas other than H, leaving the H in pure compressed condition.

Dispersoids, colloid powder. H. PLAUSON. Can. 226,634, Nov. 28, 1922. Dispersoids are prepd. by intensively mechanically disintegrating a sol. colloid gel in a non-solvent to yield a colloidal soln. of the sol type. A dispersion accelerator or an emulsifying agent such as a soap may be added.

Bleaching. G. ORNSTEIN. Can. 226,826, Dec. 5, 1922. Cl is introduced into water to produce a soln. of HOCl and free HCl and the material to be bleached is submitted to the action of the soln. at substantially the time of the production of the HOCl. The amt. of water used relative to the Cl is sufficient to cause the reversible reaction $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl}$ to go substantially entirely to the right.

Bleaching. G. ORNSTEIN. Can. 226,827, Dec. 5, 1922. In the prepn. of the bleach soln. of pat. 226,826 (above) sufficient basic material which will combine with the HCl formed in the soln. but not the HOCl is supplied to the soln. which is very dil.

Bleaching. G. ORNSTEIN. Can. 226,828, Dec. 5, 1922. Cl and water are mingled in the presence of an amt. of Na₂CO₃ which will react with the HCl produced in the hydrolysis of the Cl to form a neutral chloride and NaHCO₃ without also acting upon the HOCl produced in the hydrolysis, the amt. of water used being sufficient to give a soln. of great diln. The material to be bleached is submitted to the action of this soln.

Bleaching fluids. DEUTSCHE SOLVAY-WERKE AKT.-GES. IN BERNBURG. Ger. 306,193, June 19, 1918. Two solns. are prepd. by the action of 1 and of 2 mols.,

resp., of Cl on 1 mol. of Na_2CO_3 . Mixing these 2 solns. gives a more stable bleaching soln. with rapid action.

Filaments from basalt. P. DHB. U. S. 1,438,428, Dec. 12. Filaments for making textile fabrics, cables or cords are prepd. by melting and drawing basalt.

Porous material. M. O. SEIN. Can. 225,944, Nov. 14, 1922. Water is introduced into slag heated to approx. 1400° and an intimate mixt. is rapidly formed to produce a foam the temp. of which will be approx. 1000° . The foam is removed and cooled to solidification whereby the foam structure is maintained.

Reducing agents. C. S. BRADLEY. Can. 225,820, Nov. 14, 1922. A reducing agent contg. FeS and CaS is produced by heating together pyrite and burnt lime.

Phenolic condensation product. L. H. BAEKELAND. U. S. 1,439,056, Dec. 19. A phenyl ester such as phenyl phosphate or cresyl phosphates is added to phenolic condensation products to the extent of 5-60% to increase their plasticity.

Artificial pearls. J. PAISSEAU. U. S. 1,438,395, Dec. 12. A ball of enamel or similar material is covered with a mixt. of cellulose acetate or nitrocellulose solu. and fish scale and then dipped in alc. to take the solvent out of the agglutinant and effect coagulation upon the coated article.

Carbon black. C. MATLOCK. U. S. 1,438,542, Dec. 12. Hydrocarbon gases together with an insufficient amt. of air for their oxidation are introduced into hot combustion products, to effect partial combustion of the hydrocarbons; gases and C are withdrawn from the combustion zone and the C is sepd. after cooling somewhat but at a temp. above the dew point of associated condensable vapors.

Lampblack. W. H. FROST. U. S. 1,438,032, Dec. 5. Tar, pitch or a similar hydrocarbon material is diffused into a combustion chamber together with air and steam and a portion of the hydrocarbon material is burned to effect decompn. of another portion. Free C and gas are discharged into a shower of H_2O close to the point of highest temp.

Phonograph disc records. J. P. WRIGHT. U. S. 1,438,078, Dec. 5. Laminations of fabric treated with a phenolic condensation product are reinforced by an intervening layer or backing of woven metal.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Anomalies in the expansion of glasses. PIERRE LAFON. *Compt. rend.* 175, 955-8(1922).—The curves showing the expansion of glass may be divided into 4 parts: (1) a linear part giving the ordinary coeff. of expansion; (2) a part in which irregular effects occur owing to annealing; (3) a reversible change of vol.; (4) a part in which the glass becomes soft and finally molten. It is claimed that the reversible change (3) is due to an allotropic change in the amorphous silica similar to that which takes place in melted S.

E. D. WILLIAMSON

The application of calorizing to glass making processes. S. F. COX. *Glass Industry* 3, 243-5(1922).—Calorized gas burners, structural shapes and supports of furnaces, recuperator tubes, valves and dampers, bolts and accessories and pyrometer tubes for leers are suggested.

J. B. PATCH

A modern annealing cycle. W. O. AMSLER. *Nat. Glass Budget* 38, No. 29, 1,

13, 24-5, 27(1922); 3 figs.—The work of the government glass chemists on optical glass during the war is applied to the annealing of commercial bottles in the modern muffle lehr.

J. B. PATCH

From manganese to selenium. I. E. ADAMS. *Glass Industry* 3, 219-20(1922).—Instructions are given for changing a tank of glass from one decolorizer to the other. The following batch is included for narrow-neck machine-made bottles: sand 1000, soda 390, burnt lime 110, arsenic 2, borax 2, cullet 700, decolorizer mix as needed.

J. B. PATCH

Modern glass-factory equipment. W. S. MAYERS. *Glass Industry* 3, 221-3 (1922); 4, 7-8(1923); cf. *C. A.* 16, 4033.—Air compressors, blowers, conveyors, and bins for the storage of raw material are discussed. Bins of concrete or tile are recommended, together with pneumatic systems for unloading of soda ash and lime.

J. B. PATCH

Measurements on the gases evolved from glasses of known chemical composition. J. F. HARRIS AND E. E. SCHUMACHER. *Ind. Eng. Chem.* 15, 174-7(1922).—Glasses whose compns. run high in alkali give off more gas during their heat treatment than do those of lower alkali content. A definite relation appears to exist between the amt. of water vapor held by a glass and its alkali content. A relation, although not as pronounced as that mentioned above, appears to exist between the amt. of CO_2 held by a glass and its alkali content. Adsorbed CO_2 seems to be held to a glass primarily by primary valence forces. Adsorbed permanent gases seem to be held to glass primarily by secondary valence forces. Glass relatively free from absorbed gas can be produced by heating the glass during its melting process to a sufficiently high temp. A bibliography of 39 titles follows the article.

J. B. PATCH

Deposition of copper upon glass. *Metal Ind.* (London) 21, 606(1922).—A permanent deposit of Cu, which may later be either lacquered or varnished, is made as follows: Heat 1 part of freshly distd. phenylhydrazine and 2 parts of pure H_2O until the soln. is clear. To this add a warm soln. of $\text{Cu}(\text{OH})_2$ in NH_4OH , prepd. as outlined below. The $\text{Cu}(\text{OH})_2$ is converted into the cuprous state with evolution of N_2 . A hot 10% soln. of NaOH is now added with const. stirring until a slight ppt. of CuOH is formed. The glass upon which the deposit is desired, having previously been well cleaned, is then dipped into the soln. when a bright thin Cu deposit will be formed. This deposit is then washed for 1 hr. in running H_2O , then in MeOH, and finally in ether, after which it will be sufficiently permanent to withstand lacquering or varnishing. The phenylhydrazine used must have been freshly distd. under reduced pressure if success is to be obtained. The soln. of $\text{Cu}(\text{OH})_2$ in NH_4OH is made by first dissolving ordinary CuSO_4 in H_2O , then pptg. the $\text{Cu}(\text{OH})_2$ by the addn. of a soln. of NaOH in the usual way. This ppt. is filtered off, washed with warm H_2O , and dissolved in NH_4OH , when the characteristic deep blue soln. of $\text{Cu}(\text{OH})_2$ in NH_4OH is obtained.

O. P. R. OGILVIE

Pyrex glass as a material for chemical plant construction. A. B. MARSHALL. *Ind. Eng. Chem.* 15, 141-4(1923).—A description of the development of Pyrex for industrial use particularly in chem. manuf. Tables of properties and sp. applications are included.

A. E. MARSHALL

Sir William Crooke's anti-glare glasses. J. H. GARDNER. *Chem. News* 125, 375(1922).—Historical.

J. B. PATCH

Ceramic firing in electric furnaces. E. L. SMALLLEY. *Trans. Am. Electrochem. Soc.* 42 (preprint).—Properly designed elec. furnaces are entirely dependable for ceramic firing at any temp. up to 1100° . Elec. furnace firing has been used to advantage in the manuf. of grinding wheels, china, glassware, and bifocal lenses.

L. J.

Clay in 1921. JEFFERSON MIDDLETON. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. II, 105-10(preprint No. 18, publ. Sept. 20, 1922).

E. J. C.

Historical sketch of the pottery industry. R. H. MINTON. *N. J. Ceramist* 2, 179(1922).

C. W. PARMELEE

Drying of clayware. ANON. *Brit. Clayworker* 31, 285(1922). O. P. R. O.

The occurrence of vanadium in ceramic raw materials and ware and its effect upon the fusibility as well as the color and formation of scum on a pure kaolin and a brick clay. O. KALLAUNER AND I. HRUDA. *Sprechsaal* 45, 333-5, 345-9(1922).—A large no. of minerals contain V in small amts. and among these is clay. Seger pointed out that KVO_3 often causes a scumming and yellow discoloration on brick clays. A study was made of the effect of V_2O_5 on fusion, discoloration and scumming. V_2O_5 in small amts. does not affect the fusibility of kaolin but in larger amts. acts as a strong flux as is shown below:

Kaolin	100	99	95	90	80	60	40	20	0%
V_2O_5	0	1	5	10	20	40	60	80	100%
Fusion cone.....	35	34	33	32	30	15	5a	08a	675°

The V_2O_5 causes a yellow discoloration when present in quantities as low as 0.1%. This discoloration may be partly reduced by the addn. of $BaCO_3$ or $Ba(NO_3)_2$. As low as 0.001% V_2O_5 may cause scumming. This scumming may be reduced by firing with a reducing kiln atm. and by the addn. of Ba or Ca compds. as is shown below. All tests were made on a mixt. of 99% kaolin and 1% V_2O_5 , and the amt. (in mg.) of sol. V_2O_5 after the different treatments was used to compare the different methods.

	No treat- ment.	2 equivs. 5% $BaCO_3$	2 equivs. 5% $CaCO_3$	2 equivs. 5% $PbCO_3$	2 equivs. 5% $MnCO_3$	2 equivs. 5% $BaCO_3$	1 equiv. $Ba(NO_3)_2$
Dry	0.591	0.542	0.219	0.443	0.223	0.034
Oxid.							
500°	0.243	0.025	0.490	0.132	0.204	0.024	0.048
700°	0.021	0.098	0.141	0.014	0.021	0.023	0.038
900°	0.076	0.115	0.258	0.049	0.103	0.051	0.055
1100°	0.095	0.080	0.063	0.022	0.084	0.013	0.058
Reduc.							
500°	0.143	0.012	0.400	0.023	0.199	0.024	0.048
700°	0.046	0.026	0.068	0.029	0.116	0.026	0.029
900°	0.048	0.006	0.035	0.016	0.064	0.021	0.020
1100°	0.078	0.069	0.060	0.009	0.017	0.016	0.066

H. G. SCHURECHT

Unique development of modern chemical stoneware. P. C. KINGSBURY. *Chem. Met. Eng.* 27, 1226-31; *Chem. Age* (N. Y.) 30, 551-4(1922).—Pumps, fans, coils, filter presses and many other shapes are now made from stoneware. Carefully selected clays are mixed and aged from 2 to 5 yrs. in the plastic state. A typical body compn. is SiO_2 73.23, Al_2O_3 22.27, Fe_2O_3 0.58, CaO 0.58, MgO trace, K_2O 2.02, Na_2O 1.42, loss on ign. 0.06%. The compn. of the salt glaze is SiO_2 66.80, Al_2O_3 20.65, Na_2O 12.55. Phys. properties are tensile strength 1,000-2,200 lbs. sq. in., compressive strength 25,000 lbs. sq. in., modulus of elasticity 6,000,000-9,000,000, thermal cond. 0.55-0.60 B. t. u. sp. heat 0.2, sp. gr. 2.17, coeff. of linear expansion 0.000,003-0.000,005. R. J. M.

Tile- and brick-making materials of Nigeria. ANON. *Bull. Imp. Inst.* 20, 302-10 (1922).—Two samples of clay ("old" and "new") from Nigeria were examd., "Old" clay is suitable for the manuf. of bricks and can be used either alone, or mixed with "grog" (the raw clay fired at 1,000° for 6 hrs., and ground to 8-mesh) or with "new" clay. For the production of roofing tiles the clay should be either ground or washed to reduce the amt. of coarse siliceous matter. The "new" clay lacks binding qualities and could not satisfactorily be used alone for brick-making; but it could be used if

mixed with a certain proportion of "old" clay. For tiles, "new" clay cannot be used alone, but a product of fair quality can be obtained from mixts. of "new" and "old" clays, or by adding 2% of portland cement to "new" clay. The latter can also give satisfactory tiles if it is washed and mixed with a suitable quantity of "grog." A. P.-C.

Burning roofing tile. ANON. *Brit. Clayworker* 30, 279-80(1922).—Tile burned in continuous kilns are equal to those fired in periodic kilns. The burning schedule is: smoking 3 days, preheating 5 days, full fire 3 days, cooling 5 days and setting and drawing 2 days. By using a kiln twice the usual length it is possible to increase the rate of fire travel in the same proportion.

H. G. SCHURECHT

Brick for forges and annealing furnaces. ANON. *Brit. Clayworker* 31, 154-5 (1922).—Brick for the sides and top should resist spalling while those on the bottom should resist slagging action. The most suitable are grog firebrick. SiO_2 brick fail because they are not resistant to spalling. Special refractories are too expensive. No. 2 firebrick are amply refractory. The firebrick for the hearth should be fine in texture, rather dense on the surface and porous inside. Even for the hearth it is seldom necessary to use firebrick of high refractoriness. Strength is more important. Machine-made firebrick are quite satisfactory for the hearths of forges as they have a close-textured surface resistant to slags, while their interior is porous.

H. G. S.

Standardization of enameled apparatus for chemical purposes. E. P. POSTE. *Chem. Met. Eng.* 27, 1016-9(1922).—Full information would enable the manufacturer to give better service.

R. J. MONTGOMERY

Fireclay refractories. A. G. WIKOFF. *Chem. Met. Eng.* 27, 969-71(1922).—The products of the Laclede-Christy Clay Products Co. are briefly described.

R. J. M.

Clay and cement tubing (BURCHARTZ) 20. Deflocculating clay (U. S. pat. 1,438-587) 30.

Metallic decorations on china or glass. E. WARRIN. U. S. 1,438,799, Dec. 12. A design is printed upon the article to be decorated and the portion of the article not to be decorated is covered with an acid-resisting paste. The article is then immersed in HF soln. and the etched portion is filled with a Ag soln. which is subsequently fused into the material and then successively electroplated with Cu and Au.

Material for furnace walls. J. H. GRAY. U. S. 1,439,410, Dec. 19. Bricks for furnace walls are formed mainly of a carbonaceous material such as a calcined anthracite mixt. with a facing layer of another refractory material more resistant to oxidation, e. g., MgO, clay and SiO_2 , Cr ore or zirconia.

Safety-tread tile. M. F. BEECHER. U. S. 1,439,285, Dec. 19. Si carbide granules forming the main portion of the tread surface of tiles are united into an integral porous mass by a porcelainic bond.

Ceramic electric insulating material. J. A. JEFFERY. U. S. 1,438,598, Dec. 12. Ceramic insulating material is formed from a raw batch composed of a calcined mixt. of clay, alumina and talc or feldspar mixed with raw clay. The clay of the calcine is selected so that it matures at the temp. of the formation of sillimanite and the raw clay is of such a nature that when heated by itself it matures at the temp. at which the ceramic mixt. matures.

Refractory material for high-temperature apparatus. H. B. CLAPP. U. S. 1,437-584, Dec. 5. A mixt of chromite 85 and ferro-Si 5 parts reduced to small particles and associated with a binder, e. g., Na silicate soln. 10 parts, is used for making linings of portable gas producers or other articles exposed to high temps.

Refractory ceramic ware. J. A. JEFFERY. U. S. 1,438,590, Dec. 12. A refractory material adapted for furnace linings or saggars is formed from a raw batch comprising a granular refractory material such as Si carbide and Edgar's plastic kaolin or a clay of like character.

Bonded alumina refractory material. M. F. BECHER. U. S. 1,439,286, Dec. 19. Cryst. Al_2O_3 grains contg. slag and oxidation impurities are integrally united by a vitrified ball clay material so that the grains are substantially in contact and shrinkage of the article during firing is minimized. Articles such as firebricks may be thus formed and are fired above cone 12 until any permanent vol. change due to expansion of the material has been completed.

Fused ceramic bearing. T. G. McDOUGAL and S. J. McDOWELL. U. S. 1,438,188, Dec. 12. Annular bearings for speedometers or other instruments are formed of a fused ceramic material prepd. from a mixt. of feldspar and clay.

Enamel-coated writing tablets. R. ZULAUF. U. S. 1,438,154, Dec. 5. A first enamel coating of ordinary compn. is applied to sheet Fe and "stoved" and a finishing enamel is then "stoved" upon the first coat. The finishing coat is prepd. by grinding a fused enameling mixt. of ordinary compn. with a considerably larger addn. of clay than usually employed. This second coat gives a dull or mat finish.

Continuous updraft vertical shaft lime kiln. V. ARNOLD. U. S. 1,439,597, Dec. 19.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILBY

Caustic magnesia cement. ANON. Bur. of Standards, *Circ.* 135, 1-14(1922).—General information concerning this type of cement is given, including discovery, early history, methods of manuf., and use for flooring, stucco, and ship decking. Considerable confusion has arisen because of the variety of names under which the material has been sold and variations in its quality and behavior. Recently a committee representing a Western organization of producers and two of the Federal bureaus has been organized to write specifications. Color, fineness, time of set, modulus of rupture, and constancy of vol. are being considered. Chem. requirements have been omitted.

J. C. WYRR

Cement kiln insulation. P. C. DURBIN. *Concrete* (Mill Section) 22, 2-4(1923).—The advantages of an efficient insulating material in a cement kiln are: (1) a marked saving of fuel, (2) better working conditions, (3) longer life of shell and auxiliary equipment, (4) longer life of refractories, (5) more uniform distribution of heat, (6) ease of temp. control and (7) conservation of unused heat for power production. J. C. WYRR

Integral waterproofings for concrete. A. H. WHITE. *Ind. Eng. Chem.* 15, 150-53 (1923).—Some of the reaction products of the hydration of cement are colloidal and these remain in this condition for at least 20 yrs. When concrete is in contact with water, the colloids take up water and swell, thereby causing the concrete to expand and at the same time preventing more water from entering. When concrete dries out the reverse process takes place and there is a corresponding contraction. Water coming to the surface contains $Ca(OH)_2$ in soln. In presence of CO_2 in the atm., this $Ca(OH)_2$ becomes $CaCO_3$ and seals the ends of capillary openings of the concrete, thus acting as a waterproofer. At the Univ. of Michigan the effect of several waterproofing compds. on 4' by 4' by 6-in. specimens (1:3 mortar) was studied. The compds. were hydrated lime, clay, petroleum residua, and insol. soaps. The results indicate lime and clay should not be considered as waterproofing agents. Oil decreases the absorption,

but an objection to its use is that in time some of it comes out of the concrete. Insol. soaps decrease the absorption and frequently decrease the strength also. In some cases, however, specimens contg. small amts. of insol. soaps show increased strength. Such a specimen when stored in air dries out more slowly than an untreated specimen, and the water is therefore retained for a longer time, thus favoring the formation of colloids and a corresponding increase in strength. J. C. WYRR

Clay and cement tubing. H. BURCHARTZ. *Mit. Materialprüfungsamt* 39, 15-53 (1921).—New data are given for compression strength and resistance to internal pressure. The stability towards acids of clay tubes and the absorption of H_2O and permeability to H_2O of both clay and cement tubing are also given. The results of each individual test are reported in detail because the deviations for tubes of similar shape and material were so large that mean values are considered unreliable. Ruptures were variable, some occurring longitudinally, others both longitudinally and transversely with rough surfaces of varying colors. The tests included tubes of clay and stoneware of circular cross-section, cement of circular cross-section and flat base, cement without base, cement without joints, cement of egg-shaped cross-section and special forms. No law was found giving any relation between size and strength. All results are in kg. per sq. cm. *Clay tubes. External pressure.*—The breaking load was 2500-4000 for 80% of the tubes, with 6% below this range. The mean values of all tubes (20 to 100 cm. inside diam.) lay between 3180 and 4090. The mean of all the av. values was 3580. *Internal pressure.*—The mean value (tangential stress) of all tubes varied from 34.3 to 77.7. The mean of all av. values was 59.7. *Cement tubes. Circular tubes.*—The breaking load was essentially 2500-5500, with only 8% below this range and 16% above. The highest breaking loads were 7600 and 7620 for 2 tubes of 40 cm. diam. The mean values for the various sizes varied from 2630 to 5290 and the mean of all averages was 4150. *Egg-shaped tubes.*—The breaking load was for the majority 4000-7000 with 17% under and 21% over this range. A tube of 70/105 cm. inside-outside diam. gave 11,010. The mean values of all sizes were 4260-8200, and the mean of all averages was 5270. By the standard test, the soly. of most of the clay tubes in H_2SO_4 was 0.04-.08%, with 1 case of 0.23%. Cement tubes immersed in 0.5% $HOAc$, HCl , H_2SO_4 and HNO_3 showed surface attack, due to the Ca compds. present. H_2O absorption was 2.1-5.3% for clay tubes and 7.1-7.7% for cement tubes. Cement tubes were found both porous to H_2O and waterproof. Clay tubes were those with porous surface and a H_2O absorption up to 10% and stoneware tubes as those with a vitrified surface and H_2O absorption not over 5%. C. C. DAVIS

Tests on the double burning of lime, and the value of cements of high hydraulic index. F. B. JEANNERET. *Rev. mat. constr. trav. pub.* 158, 213-5(1922).—Binders of high hydraulic index show their max. properties when they have a $CaCO_3$ content of 72-75%. LOUIS NAVIAS

An impact test for gravel. F. H. JACKSON. *Proc. Am. Soc. Testing Materials* 22, II, 362-74(1922). E. J. C.

Sand and gravel in 1921. L. M. BRACH. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. II, 147-54(preprint No. 24, publ. Nov. 6, 1922). E. J. C.

Coal-tar and water-gas tar creosotes: their properties and methods of testing. ERNEST BATEMAN. U. S. Dept. Agr., *Bull.* 1036, 1-114(1922).—A review is given of the compn. and of the chem., physical and toxic properties of coal-tar and water-gas creosotes; of the compn. of tars and their methods of manuf.; and of the theory of the mechanism of the protection of wood by creosote solns. A comparison of the properties of authentic coal-tar creosotes with those of authentic water-gas creosotes shows that there is no sharp line of demarcation between their physical constns. Methods are given

for testing creosotes and also the official specifications now in force by various associations.

W. H. ROSS

The processes which occur during the formation of mortars. AUGUST ZELLWEGER. *Jahrb. Phil. Fak. II, Univ. Bern* 1, 102-6(1921).—MgO and CaO were separately treated with an excess of water or of solns. of electrolytes and the velocity of slime deposition was measured. The influence of the various ions was in general the same for these oxides; it seemed to be detd. largely by the colloidal condition of the oxide. Adsorption and swelling apparently were involved in the behavior shown. The volume changes which accompany the *slaking of MgO* were studied dilatometrically. An initial expansion followed by a subsequent contraction was observed. The relative influences of various salts upon the expansion were the same as in the sedimentation expts. The final contraction was not affected by electrolytes. The influences of various electrolytes on the hardening of MgO slime were in the same order as in the preceding expts. Colloidal swelling is the first step in the slaking process and colloidal processes are responsible for the various phenomena which accompany slaking. E. W. W.

HARRIS, WALLACE R. AND CAMPBELL, H. COLIN: *Concrete Products; Their Manufacture and Use*. Chicago: International Trade Press, Inc. 238 pp.

Waterproofing cement. C. W. BALL and F. L. PILGRIM. *Can.* 226,350, Nov. 21, 1922. Cement is made waterproof and strengthened by the addn. of diatomaceous earth.

Waterproofing composition. M. W. HENDRICH. U. S. 1,437,893, Dec. 5. A soln. adapted for waterproofing *brick walls* or *concrete* is formed of $\text{Ca}(\text{OAc})_2$ and $\text{Al}_2(\text{SO}_4)_3$ and a neutral soap soln., with sufficient admixture of glue to retard pptn.

Homogeneous porous materials. M. O. SEM. *Can.* 225,943, Nov. 14, 1922. A porous material suitable for building purposes is made by forming a foam in a slag melt and rapidly lowering the temp. of the material by the action of a water-cooled roller and solidifying the material by slow cooling.

Sheet roofing material of pitch and fibrous material. R. P. PERRY. U. S. 1,438,966, Dec. 19. Roofing or "boarding" sheets are formed of fibrous material mixed with comminuted pitch, a larger proportion of pitch being used in the surface than in the interior portion of the sheet.

Impregnating wood with preservatives. W. C. ZELLER. U. S. 1,438,471, Dec. 12. A portion only of telephone poles or other lengths of wood in a closed receptacle is treated with a preservative under pressure.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

The concentration of coal by flotation. KUNO WOLF. *J. prakt. Chem.* 105, 39-49(1922).—A general paper. It outlines the practice and theory of ore flotation; states some of the problems peculiar to the flotation of coal; and describes several problems of coal utilization which have been solved by flotation. R. H. L.

Comparison of froth with Trent process. O. C. RALSTON. *Coal Age* 22, 911-4 (1922).—Tests on 5 types of Pacific Northwest coals including sub-bituminous, non-coking and coking bituminous coal, and semi-anthracite showed that with the Trent

process recovery increased and ash decreased with increasing fineness of grinding for all the coals. Combustible recovery was over 75%; ash reduction varied; a 25.9% ash coal gave a 12.2% ash concentrate, while a 13.43% ash semi-anthracite gave a 7.50% ash concentrate. Bony coals, even when ground to 300 mesh, retained a high inherent ash content in the concentrate. Conclusion: 65-mesh material under conditions more favorable to the froth-flotation than the Trent Process both give similar results for obtaining a low-ash fuel. Trent process gives higher combustible recovery while the froth-flotation process is more flexible, especially in handling bony coals.

W. W. HODGE

Analyses of Kentucky coals. Bur. of Mines, *Tech. Paper* 308, 92 pp. (1922).—Following brief discussions on (1) "Geology of the coal formations," by M. R. CAMPBELL, "Mining methods," by C. A. HERBERT, "Use and distribution of the coal produced," by F. G. TRYON, "Fusibility of ash" and "Chemical analyses of mine samples," by A. C. FIELDNER, H. M. COOPER and F. D. OSGOOD, and on "Delivered coal," by N. H. SNYDER, are to be found 69 pages of analyses.

E. J. C.

The utilization of low-grade coals at the Montrambert and de la Béraudière coal mines. ANDRÉ PIGEOT AND FRANÇOIS BLACHE. *Rev. métal.* 19, 665-71 (1922).—Coals contg. 42-45% ash and 18-20% volatile matter, which are of such a nature that they cannot be satisfactorily washed, are coked with recovery of heat and by-products; the impure coke is burned in gas producers, and the purified gas used in a gas engine. The exhaust is discharged to the atm., but could be sent to a boiler where 1 lb. of steam could be generated per kw. hr. generated by the gas motor. The app. used at the mines is described in detail.

A. P.-C.

The technic of industrial heating by means of pulverized fuel suspended in air. HENRI VERDINNE. *Rev. métal.* 19, 590-6 (Abs.) (1922).—A discussion of inflammability, fineness of grinding and limiting velocity of the particles, combustion, design of combustion chambers, and difficulties encountered in practice and of the results of Taffanel and Audibert on coal-dust explosions at expt. galleries.

A. P.-C.

Colloidal fuels: their preparation and properties. A. E. DUNSTAN. *Brit. Assoc. Advancement of Science, 4th Rept.* 1922, 380-2.—A brief note. JEROME ALEXANDER

The control of combustion. Relation between the composition of the fuel and of the flue gases. Determination of excess air. Volume of air used for combustion and volume of gases produced. G. DELADRIÈRE. *Rev. métal.* 19, 599-602 (Abs.) (1922).—CO₂ content of flue gases always refers to the flue gases after condensation of any H₂O which they may contain. Whatever the H₂O content of the fuel, and the amt. of H₂O added with the air required for combustion, the CO₂ content of the flue gases, obtained by complete combustion without excess of air, is const. Such flue gases are "neutral." Let *C* be the vol. of CO₂ obtained by combustion of 1 m.³ (of gaseous) or 1 kg. of (liquid or solid) dry fuel; *B* the vol. of neutral flue gases obtained from 1 m.³ or 1 kg. of fuel; *C'* the vol. of CO₂ in 1 m.³ of flue gases from the combustion under investigation; *B'* the vol. of neutral flue gases which would be obtained by combustion of 1 m.³ of flue gases from the combustion under investigation. Then $C/B = C'/B'$. This relation is absolutely general and can be applied in all cases. D. shows how to calc. the amt. of excess, the vol. of flue gases produced per unit of fuel, and gives examples showing how these data can be used for checking up the accuracy of fuel and flue gas analyses for making up heat balances.

A. P.-C.

The B. t. u. chart. C. J. LOHMAN, JR. *Chem. Met. Eng.* 27, 1031 (1922).—This chart is so constructed as to indicate directly the heat value of a fuel, given the corrected temp. rise of the calorimeter, thermometer and the % of moisture in the charge.

H. L. OLIN

Tables and charts for natural gas users. R. P. ANDERSON. *Chem. Met. Eng.* 27, 1039-40(1922).—Curves are given showing CO₂-excess air relationships and CO₂-excess air heat losses for various natural gases.

H. L. OLIN

Manufactured gas and by-products in 1920. R. S. McBRIDE. U. S. Geol. Survey, *Mineral Resources of U. S. 1920*, Pt. II, 439-97(preprint No. 35, publ. Dec. 12, 1922).

E. J. C.

Water-gas reactions. R. T. HASLAM, F. L. HITCHCOCK AND E. W. RUDOW. *Ind. Eng. Chem.* 15, 115-21(1923).—A study was made of the formation of water gas through a range of temps. from 650° to 1200° by varying the steam pressure in the generator and using 2 kinds of C. The app. and method are described. The essential reactions are: (A), $C + H_2O = CO + H_2$; (B), $C + 2H_2O = CO_2 + 2H_2$; (D), $C + CO_2 = 2CO$. These reactions take place at the surface of the C and are monomol. The rate of formation of CO₂ at temps. below 900° is $CO_2 = 0.5 [H_2O - (H_2O)^2]$ and at temps. above 900° $CO_2 = 0.47 [H_2O - (H_2O)^{1.35}]$. By taking the rate of reaction B as unity, it is found that at temps. below 900°, reaction A is practically non-existent and the velocity const. of reaction D is 2, and at temps. above 900° the velocity const. of reaction A is 1 and that of D 2.18, indicating that at high temps. A takes place more rapidly and D less rapidly than B, but that at all temps. the main reactions are B and D. The effect of undecompd. steam in the CO:CO₂ ratio is shown to be the controlling factor rather than the temps. at which the reactions take place. An increase in pressure under which a water-gas generator is operated may be used to obtain the same effect as an increase in the time of contact, in the depth of fuel bed, or in an increase in temp. Thus a 3-fold increase in pressure will produce almost a 3-fold increase of water gas without a change in compn. of fixed gases.

J. L. WILEY

Fused-ash gas producer. EMMANUEL SERVAIS. *Rev. métal.* 19, 596-9(Abs.) (1922).—With Ruhr coke in lumps of 10-60 mm. contg. 12-15% ash and moisture (compn. of ash about 48 SiO₂, 36 Al₂O₃, 9 Fe₂O₃, 3 CaO, and 4% undetd.), the producer worked perfectly for a few hrs.; but after about 15 hrs. it began to clog up because of premature fusion of the flux and ash of the coke due to excessive temp. (1,600° or over). Steam was injected, the reduction of which absorbed the excess heat, the amt. being calcd. to bring the temp. down to about 1,000-1,100°. In practice this is obtained by starting up the producer as usual, and then gradually increasing the amt. of steam until the gas has a CO₂ content of 1.5-2.0%. The approx. compn. of the resulting gas is CO 31-32, H₂ 6-8, CO₂ 1.5-2, N₂ 53-60%, calorific value 1,140-1,200 cal. Lump CaCO₃ is not satisfactory as flux, as it does not readily react with the SiO₂ of the ash. A blast-furnace slag contg. SiO₂ 30, Al₂O₃ 15, CaO 42, MgO 6, Fe₂O₃ and MnO 7% was used; but instead of the amt. theoretically required to make the ash fuse at the temp. prevailing in the crucible, about 10-12% (on the wt. of fuel) was used in order to have a sufficient amt. of heat in the crucible. The resulting slag consisted of SiO₂ 38, Al₂O₃ 26, CaO 32, MgO 2, Fe₂O₃ 1, MnO 1%, and was drawn off at about 1500-1600°. A certain amt. of high-Si iron was also produced. The blast-furnace slag was later replaced by the producer slag, to which was added pulverized limestones. The air was blown through 8 tuyères at about 250°. Preheating the air is not necessary but is preferable, as the ash can then be drawn off more easily and also more steam can be injected, thus raising the calorific value of the gas. The producer is very easy and cheap to operate, and there is practically no danger of its blocking. An outline of the heat balance is given.

A. P.-C.

Carbureting with low-grade oil. H. VITTINGHOFF. *Gas Age-Record* 51, 87-70 (1923).—A description of a new water-gas plant at Fall River, Mass. adapted to use low-grade Mexican petroleum.

J. L. WILEY

Suction gas for power purposes. II. R. N. LEWIS. *Commonwealth Eng.* 10, 130-4(1922).—The operation of a producer-gas plant is explained, and the advantages and disadvantages of the various types of steam-generating app. are given. L. favors the internal coil vaporizer, although the internal reservoir type is the one most generally used, as it requires a minimum of care and attention. The fuel requirements for a suction plant running 24 hrs. per day av. about 1 lb. per h. p. per hr. J. L. WILEY

The future of the electric gasification of fuels. A. HELFENSTEIN. *Chaleur et industrie* 3, 1522-6(1922); *Fuel* 124, 223; cf. C. A. 16, 1497.—The advantages of elec. heating in the gasification of fuels are discussed from the standpoint of control of operation, quality of gas produced, and quantity of elec. energy required. C. C. D.

The production of metallurgical coke from non-coking coals. M. DOLCH. *Glückauf* 58, 772-6(1922).—A discussion of the work of Lierg (C. A. 16, 3194) and of the new metallurgical fuel made by coking anthracite fines with coal-tar pitch, called "Anthraccoal" (cf. C. A. 15, 3733). C. C. DAVIS

Survey of the application of the rare metals and rare earths in the (gas) lighting industry. OELKRR. *Edel-Erden u. Erze* 4, 5-6(1922).—A review of Ger. patents. E. J. C.

Deposits in gas pipes and meters. R. L. BROWN. *Gas Age-Record* 50, 571-4(1922).—Line 7 of C. A. 17, 201 should be corrected as follows: The O autoxidizes the unsatd. hydrocarbons of which indene and styrene constitute the great part of those present. J. L. WILEY

Enriching mine gases in methane. E. BERL AND O. SCHMIDT. *Z. angew. Chem.* 35, 633(1922).—The utilization of 1 to 2% of CH₄ in mine ventilating gases is of increasing com. importance. Adsorption on agents of large area, followed by fractional heating, can give gas mixts. contg. 6.2-12.7% CH₄ suitable for use in gas engines, and the hot exhaust from the latter can be used to heat the adsorbent. 100,000 cu. m. CH₄ daily, if used in a gas engine at an efficiency of 20-25%, would give 10,800-13,400 h. p.; if used in steam engine-generator sets it would yield about one-half this amt. Activated C was treated with moist air contg. 2% CH₄ until satd. with the latter. During this process some of the easily combustible hydrocarbons oxidize to CO₂, which can be fixed later, if necessary. The adsorbed gases were expelled (a) with steam, or (b) by heating to 100°, later to 175° and finally with steam, yielding mixts. contg. 5.9-8.0%, 1.85, 2.50 and 8.60% CH₄, resp. Some 97% of the CH₄ present is recovered. W. C. EBAUGH

Benzene. J. BUIJS. *Het Gas* 42, 318-24(1922).—The question is discussed as to whether it is more economical to remove from illuminating gas a larger or a smaller part of the C₆H₆ contd. therein. Advantages and disadvantages are considered. Two systems, A (gas work) and B (coke furnace), are compared. A removes about 5 kg. benzene per ton of coal, B about 8 kg., both by washing with tar oils. Owing to the larger output of benzene the second system, of course, pays better, although the gas obtained is poorer. R. BREUNER

The forms of sulfur in coke. A physico-chemical study of the sulfur held by carbon at high temperatures. A. R. POWELL. *J. Am. Chem. Soc.* 45, 1-15(1923).—A phase-rule study of the C-S complex, (1) with a system of pure sugar charcoal with S added at high temps. and (2) with coke itself. The method of attack was based upon the following known phase-rule relationships: (1) A compd. at const. temp. exhibits a const. dissoc. pressure and its isotherm showing, in this case, the vapor pressure of S at different concns., would be a straight horizontal line; (2) a solid soln. if sufficiently dil. follows Henry's law and its isotherm is a straight slanting line; (3) while the phase rule does not hold for adsorbed substances, the isothermal curve has a characteristic shape,

the concn. of the gaseous phase being in general an exponential function of the amt. adsorbed. Knowing, therefore, the initial concn. of the S, the amt. removed during each stage of the run and the partial pressure of S during the stage, it was possible by a study of the pressure-concn. isotherm to det. the character of the combination. Conclusion: In the C-S system S occurs in 2 forms, (a) adsorbed free S and (b) S in solid soln. Coke made in the lab. by the rapid heating of coal contains in addn. FeS; that made slowly in com. ovens contains but 2 forms, viz., the solid soln., or S adsorbed in such a way as to give the same properties as the solid soln., and FeS.

H. L. OLIN

Structure of coke; its origin and development. GEO. BEILBY. *J. Soc. Chem. Ind.* 41, 341-71 (1922).—See C. A. 16, 2590.

C. T. W.

Coke and by-products in 1919-1920. R. S. McBRIDE AND F. G. TRYON. U. S. Geol. Survey, *Mineral Resources of U. S. 1920*, Pt. II, 361-437 (Preprint No. 34, publ. Oct. 18, 1922).

E. J. C.

The mechanical production of coke. A. THAU. *Stahl u. Eisen* 42, 1838-43, 1888-74 (1922).—A short description of the last two years' progress and economy in oven arrangement, platform design, and mech. shovels. New developments are discussed especially the cooling of coke with inert gases to increase the C content.

W. A. MUDGE

Occurrence and uses of peat in the U. S. (SOPER, OSBON) 8. Photosynthesis and the possible utilization of solar energy (SPÖHR) 13. Gas useful in heat-treating room (SMITH) 9. Refractory material for high-temperature apparatus (U. S. pat. 1,437,584) 19. Purifying liquors contaminated with phenol (U. S. pats. 1,437,394 and 1,437,401) 14.

SYNDICAT D'APPLICATIONS INDUSTRIELLES DES COMBUSTIBLES LIQUIDS: Les combustibles liquids et leurs applications. Paris: Gauthier-Villars et Cie. 621 pp. Reviewed in *Proc. Am. Soc. Civil Eng.* 47, 973 (1921).

Mixed liquid fuel. G. E. GRAY. U. S. 1,438,823, Dec. 12. A hydrocarbon liquid such as kerosene or a heavier petroleum distillate is sprayed in mixt. with acetone over pieces of metal, stone or coke or other inert surface-extending material in a chamber to which a gaseous hydrocarbon material such as natural gas is also supplied, to form a fuel mixt. adapted for use in internal combustion engines.

Hydrocarbon motor fuel. L. DE FLOREZ. U. S. 1,437,045, Nov. 28. Gas oil, kerosene or other hydrocarbon liquid less volatile than gasoline is cracked by heating to 500-600° under 5 atm. pressure and products volatile at 140-220° are sepd. by passing them through a dephlegmator at atm. pressure. Gases and vapors from the dephlegmator are passed through a condenser at 25-30° and the condensate and gases are then compressed together at 10 atm. to effect partial liquefaction and blending.

Apparatus for vaporizing liquid fuels. A. H. EBOV. U. S. 1,437,587, Dec. 5. Liquid fuels, e. g., a fuel adapted for running an internal combustion engine, are vaporized completely from the surface of a rotating disk, to the depressed central portion of which the liquid fuel is fed.

Liquid-fuel burners. A. W. SOUTHEY. Brit. 185,877, June 25, 1921. A liquid-hydrocarbon burner comprizes a wick having a considerable portion of its side surface exposed, sufficient air being admitted to the lower part and insufficient air to the upper part of the exposed portion to support combustion so that the hydrocarbon fed to the

upper part is vaporized by the heat of the flame at the lower part. The mixt. of vapor and combustion products with air is subsequently burnt as a Bunsen flame.

Montan wax from brown coal. H. PLAUSON. U. S. 1,437,775, Dec. 5. See Can. 220,516 (C. A. 16, 2982).

Peat. C. W. G. CLEWLOW. Brit. 186,690, July 1, 1921. An app. for treating macerated peat pulp which has preferably undergone a preliminary treatment by means of which a portion of its water content has been rendered mechanically separable, preferably such as is described in 183,566.

Gas manufacture. G. HELPS. Brit. 181,403, Dec. 10, 1920. Coal is treated in a combined gas-producer and retort to produce a rich gas which is collected and a producer gas which is burned in a sep. setting surrounding other retorts. The producer gas may also be passed through the externally heated coal retorts or mixed with the rich gas after it leaves these retorts. A low-grade gas enriched in the manner described in 181,404 (cf. following pat.) may be led into the coal retorts. A suitable app. is specified. Cf. 4572, 1913 (C. A. 8, 2798) and 101,306.

Gas manufacture. G. HELPS. Brit. 181,404, Dec. 10, 1920. Low-grade gases are enriched by being superheated, preferably in a bed of incandescent fuel, and passed through a retort contg. coal shale, etc. Gas from a producer is superheated by passage through a bed of incandescent coke previously blown up with air from an inlet, the waste gases passing by a pipe to a jacket surrounding a retort and escaping by an outlet. The superheated gas is passed through the retort and partly distills the fuel therein, the rich gas mixing with the low-grade producer gas and leaving by an outlet, the resulting coke falling into a discharge shoot. In another form, the retort is placed in and surrounded by the coke and the gas-superheating chamber. According to the Provisional Specification, the superheating chamber may be dispensed with and the retort heated by combustion of a part of the low-grade producer gas, or the waste gases from the blow may be used to heat up the chequer work in regenerators, which are then used to superheat the low-grade gas. Cf. 181,403 (preceding pat.).

Device for supplying fuel to gas producers. D. J. SMITH. U. S. 1,439,647, Dec. 19.

Fuel feeding apparatus for gas generators. J. E. SHARP and A. J. BASSETT. U. S. 1,439,192, Dec. 19.

Retort bench for gas production. G. H. NILES. U. S. 1,438,258, Dec. 12. Structural features.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

The petroleum industry in 1921. RICHARD KISSLING. *Chem.-Zig.* 46, 111-4, 1129-32, 1137-40, 1153-6, 1165-8(1922). E. H.

Colloidal chemistry and the petroleum industry. R. KORTSCHAN. *Kolloid-Z.* 31, 314-9(1922).—An address. The theory of colloidal dispersion of asphalt, paraffin, fluorescent substances, etc., applies to the substances generally considered to be admixed or in chem. bond with the oil. Many successful applications of colloidal chem. principles are cited and problems are pointed out. A. MUTSCHALLER

Polish and German bibliography of the Galician petroleum industry, 1875-1922. ANON. *J. Inst. Petroleum Tech.* 8, 666-87(1922). E. J. C.

Gasoline ten years hence. R. H. MCKERR. *Can. Chem. Met.* 7, 4-6(1923).—

A survey of the outlook for future supplies with a discussion of possibilities of oil shales, E. H.

The Osage oil field, Weston County, Wyoming. A. J. COLLIER. U. S. Geol. Survey, *Bull.* 736-D, 71-110(1922).—In 1921 there were about 100 wells in this region with a combined daily yield of 500 barrels of oil. The location of many of the wells is described and the relations of production to structure of the strata are indicated. The oil is light olive green in color; a deep sample gave: sp. gr. 0.822, gasoline 35.9, kerosene 16.1, gas oil 11.8, light lubricating 11.0, medium lubricating 4.1%. It is estd. that there are 175 million barrels of oil in the 12 sq. mi. of the Osage field, 96% of which is unobtainable. This is a startling commentary on the inefficiency of even the best methods of production. L. W. RIGGS

The oil shale development and the oil shale industry in Estland. A. VON ANTRUPOFF. *Z. angew. Chem.* 35, 647-51(1922).—The location of deposits is given. A relation is established between the geological formations of Estland and the shale deposits. The Kukerssche Schicht (shale) is found in layers interstratified with limestone. The shale is of animal origin (shells and fossils being found in it). The deposit contains 800 sq. km. and is estd. to contain $1\frac{1}{2}$ billion tons of shale. The shale has d. 1.2-1.6 and a chocolate brown color when moist, drying to a light grey. The material is easily lighted with a match and burns with a bright sooty flame. If powdered and atomized into a fire it burns readily. The air-dried shale contains H_2O 3.1% and bitumen 49.8%. The volatile content is 56.7%, coke 4.8 and ash 38.5. The shale is utilized for fuel, cement, gas and oil products. Its ash content is applicable as one of the constituents of cement. It yields 300 cu. m. gas per ton with 3.5% tar. The use for gas manuf. has not been profitable. Since Aug. 1921 a Pintsch retort of 9 tons capacity per 24 hrs. has proven successful and two more are being installed. The distn. is by means of internal heat, preheated flue gases supplied from distn. chamber from spent shale being used. Vapors are cooled and condensed and the remaining gas is used for fuel. No extra energy beyond that derived from the shale is needed. The amt. of oil is approx. 20% by wt. Sp. gr. of the crude oil is 1.01, viscosity (Engler) 5.5 at 50°, heat 9700 kg. cal. No paraffin is present in the oil. R. T. GOODWIN

Comparison of principles involved in existing cracking processes. L. REISS AND E. R. LÄDERER. *Refiner and Nat. Gasoline Mfr.* 2, No. 1(1923).—Cracking processes are classified as (1) cracking in stills under pressure, (2) cracking in the liquid phase in tubes under pressure, (3) cracking in the liquid-vapor phase in tubes under pressure, (4) cracking by any of the above means using steam, (5) cracking by any of the above means using fixed gases and H_2 , (6) cracking by any of the above means using chemicals, (7) cracking with the aid of internal heat, (8) cracking in the vapor phase under pressure, (9) cracking by elec. methods. Representative processes from each of the above classes are described and the merits and disadvantages of each discussed. D. F. BROWN

Contact process for filtering of petroleum products. H. L. KAUFFMAN. *Nat. Petr. News* 15, No. 3, 81-2(1923).—Acid-treated clay is obtained by treating halloysite, pyrophyllite, or montmorillonite (all occurring chiefly in Calif.) with water and grinding wet to 200-mesh. The wet earth is digested with weak acid, dried and ground to 100-mesh. Oil from the acid treat is pumped to open the top agitation tanks, agitated and 1-5% of clay added and the whole mechanically agitated with simultaneous raising of the temp. to 250-350° F. Water in the clay is desirable because the steam evolved aids agitation and forms a layer over the top of the oil, preventing oxidation. The temp. is held at the desired point with agitation until cessation of steam evolution and 10-15 min. thereafter and then allowed to settle somewhat, after which the oil is filtered. When the

filter becomes so full of clay as to impair its efficiency, compressed air is forced through to dry it. This point seems to be at $1\frac{1}{2}$ in. thickness of the cake or more. Used clay is about 50% efficient. Oil thus treated usually has the same or higher viscosity as the same oils percolating through fuller's earth. They hold their color at increased temps. longer; oil losses are very small; treating time is less; the clay can be used over with about 50% efficiency; NaOH treat for neutralization is eliminated; less acid in the acid treat is required; and a large saving in time and labor is effected. D. F. BROWN

Bog ore as an oil filtering medium. E. R. INMAN. *Oil Gas J.* 21, No. 34, 92-3 (1923).—Franklin bog ore was screened through a 16-mesh sieve, and burned by heating to a red heat, and the product used for filtering heavy Pa., Texas, and Mid-Continent crude oils. This material has excellent filtering and decolorizing properties. It is about twice as effective as fuller's earth. It can be reused almost indefinitely. Washing with gasoline, steaming, and reburning restores its efficiency. It can be used commercially and advantageously with ordinary refinery equipment. D. F. BROWN

Centrifugal oil treatment. J. H. SHEDDEN. *Petroleum Age* 11, No. 2, 26-7, 78 (1923).—If crude oil be treated with acid in centrifugal mixers followed by an alkali treat in similar app. the oil is purified to such an extent that the resultant product can be distd. into purer fractions which do not require rerunning or treating. D. F. B.

Castor machine oil: composition, value as lubricant and manufacture. H. L. KAUFFMAN. *Nat. Petroleum News* 14, No. 47, 45-6 (1922).—This oil deteriorates on standing or in the presence of moisture, owing probably to the sepn. of minute globules of Al soap. Tests were made with benzyl acetate, benzyl alc. and similar org. substances added up to 1% to render the oil more stable, but all results were negative. The value of this oil as a lubricant is doubtful. D. F. BROWN

Smackover, Bossier and Mirando crudes valuable chiefly for fuel. P. WAGNER. *Nat. Petroleum News* 14, No. 46, 27 (1922).—A 5000-cc. charge of Smackover crude to a small still, 0.6% caustic, showed a gravity of 18.6° Bé., flash 130, viscosity 555/100, steam in at 400°, over at 410° F. A 4200-cc. run with Bossier crude showed a gr. of 19° Bé., flash 205, viscosity of crude 978/100, steam in at 350°, over at 370°. A refinery test on Mirando crude (Texas) of 5000 cc. showed 21.0 Bé., flash 65, viscosity 77-100, steam in at 300° F. and over at 320°. 10% cuts of each are given. Bur. of Mines tests on Kosse (Texas) crude are given. D. F. BROWN

How our greases are made. H. L. KAUFFMAN. *Petroleum Age*, 11, No. 2, 21-2, 67 (1923).—Greases are classified as cup greases, cold set rosin greases or axle greases, railroad greases and fiber or sponge greases. Methods of manuf. and formulas for each class are given, also methods of testing. D. F. BROWN

Sangajol. R. JUNGKUNZ. *Seifensieder Ztg.* 49, 790, 803 (1922).—Sangajol is a Borneo petroleum distillate contg. cyclic hydrocarbons. It is used as a turpentine substitute. The consts. are as follows: d_{15}^4 0.7905, n_{15}^D 28.8, Eibner-Hue no. (action of 1.84 to H_2SO_4) 9.8, % of Eibner-Hue residue 17.7, b. p. 155°. Fractional distn.: 130-150° 40%, 150-180° 58%, over 180° 2%. P. EACHER

Distillation of hardwoods in Canada.* J. S. BATES. Can. Dept. Int. Forestry Branch, *Bull.* 74, 41 pp. (1922).—B. discusses the wood supply, the destructive distillation processes, and derived products. A useful table gives av. yields of products, and the heat balance. The av. fuel values in B. t. u.'s per av. lb. of product obtained are: charcoal 13,500, wood gas 2,300, tar and oils 14,000, AcOH 6800, methanol 9600, org. impurities 9600. The ordinary com. fractions (like "Royal Spirits"; Shellac spirits, etc.) prepd. from crude methanol for different industrial purposes are clearly defined. Location and capacity of the principal crude hardwood distn. plants, detailed

production statistics (including cost data), export statistics, etc., are given. Prospects for new processes are briefly discussed.

L. E. WISE

Fire and explosion hazards of petroleum and petroleum products (KATZ and SMITH.) 24. Gold in oil shales (VARLEY) 9.

KEWLEY, JAMES: *The Petroleum and Allied Industries*. London: Baillière, Tindal and Cox. Reviewed in *J. Inst. Metals* 8, 504(1922).

Cracking petroleum oils. R. B. DAY. U. S. 1,437,932-3, Dec. 5. Oil to be cracked is heated in a series of retort tubes in which steel balls are kept in motion by screw conveyors, in order to produce more uniform heating of the oil and to prevent C deposition.

Fractional condensation of petroleum hydrocarbon vapors. H. C. SMART. U. S. 1,437,889, Dec. 5. Petroleum hydrocarbon vapors are passed through an air-cooled condenser in a succession of thin annular streams in different sections of the condenser of graduated temps. (regulated by the current of cooling air) so that fractions of different b. p. are drawn off independently from the different sections of the condenser.

Washing petroleum oils. E. M. JOHANSEN. U. S. 1,438,764, Dec. 12. Petroleum or its fractions or residues from topping are successively treated with soap soln. and H_2SO_4 . The amt. of H_2SO_4 required is lessened by the soap treatment and the acid oil is treated with NaOH or other alkali to neutralize it and obtain a non-emulsifying product.

Transporting and storing petroleum oil. F. M. SEIBERT and E. T. GREGG. U. S. 1,439,451, Dec. 19. Loss of volatile liquid hydrocarbons from petroleum oils during storing and transportation in pipe lines is prevented by venting off gases and vapors from the storage or pipe system under atm. pressure, through a chamber contg. adsorbent material such as activated charcoal or silica gel.

Apparatus for cracking petroleum oils. E. C. BLASDELL. U. S. 1,437,712, Dec. 5. The pat. relates to structural features of 2 connected condensing tanks mounted above a horizontal evapp. tank.

Apparatus for distilling and coking heavy hydrocarbons. L. STEINSCHNEIDER. U. S. 1,437,566, Dec. 5. The app. is arranged to heat oil in a retort tube or series of such tubes which extend from an upper oil receptacle downward through and then outside of the fire gas passageway of a furnace. The app. is especially adapted for use with petroleum or tar.

Horizontal retort for distilling oil from oil shale. W. ALENUS. U. S. 1,438,421, Dec. 12. Spiral agitating devices and conveying arms are mounted rotatably in the retort.

Reclaiming sludge acid in petroleum refining. W. H. SIMONSON and O. MANTYUS. Can. 226,112, Nov. 21, 1922. Sludge acid is reclaimed by concg. the acid by boiling in a partial vacuum at a temp. high enough to vaporize the water but low enough to prevent the combustion of org. matter and then drawing off the acid.

Separating wax from petroleum oil. C. F. KENNEDY. U. S. 1,439,171, Dec. 19. Wax is rendered more readily recoverable from wax-bearing mineral oil by preliminary washing of the oil with a soap soln. of such a concn. as to avoid substantial emulsification.

Refining paraffin wax. T. G. DELBRIDGE. U. S. 1,438,985, Dec. 19. The cryst. structure of paraffin wax such as "slack wax" is improved by melting, washing with soap soln., cooling and sweating.

Paste from mineral oils. H. PLAUSON. Can. 226,872, Dec. 5, 1922. A mixt. of mineral oil, water and an insol. mineral agent is subjected to high speed mech. disintegration in a colloid mill.

23—CELLULOSE AND PAPER

CLARENCE J. WEST

Acetylcellulose. EMIL KNOEVENAGEL AND KARL KÖNIG. *Cellulosechemie* 3, 113-21(1922).—By the use of suitable catalysts CHCl_3 -sol. cellulose acetates can be converted into Me_2CO -sol. acetates, which occasionally show lower Cu nos. than do the original acetates. This finding is not in harmony with the hypothesis that the conversion of less sol. into the more sol. acetates is accompanied by hydrolysis. K. and K. describe in detail catalytic methods for the gradual conversion of Me_2CO -sol. acetates into very insol. varieties (insol. in AcOH and the lactates). Since this conversion involves only a very gradual sapon. of the esters (*i. e.*, only slight lowering of % Ac), K. and K. have termed the process "condensation-gelatinization" in distinction to the so-called "sapon gelatinization," which also yields highly insol. acetates, having much lower Ac nos. than the original cellulose acetates. To a certain extent these processes take place simultaneously. 15% Me_2CO solns. of cellulose acetate were treated with varying amts. of H_2SO_4 , sulfoacetic acid, or ZnCl_2 as catalysts. With the acid catalysts, gel formation occurred within 7-21 days. No gelation was noted after addn. of ZnCl_2 . The liquid exuding from the various gels was removed and analyzed at intervals after syneresis had set in. With the ageing of the gel the AcOH content of the exudate gradually increases, and the Ac no. of the gelatinous acetate decreases very slightly, indicating gradual hydrolysis (probably due to action of H_2O in the Me_2CO). The Cu no. of the gel increases, but in most cases inappreciably. The acetates obtained on gelatinization were insol. in Me_2CO , $\text{C}_2\text{H}_5\text{Cl}$, and lactic acid esters. They showed swelling, but were not peptized when treated with AcOH or 75% EtOH . When the gelatinization reaction was carried out in AcOH (instead of Me_2CO) with the same catalysts, gel formation occurred much more slowly (within 25-50 days), the time of gelation varying inversely with the concn. of catalyst. The Ac content of the gelatinized acetates varied inversely with the amf. of catalyst used, indicating hydrolysis of the ester groups during gelation. The Cu nos., however, increased comparatively little during the process. Attempts to eliminate hydrolysis during gelatinization by introducing Ac_2O into the mixt. of reagents to insure absence of H_2O , were not very successful. Gelation occurred only after 3 months, Ac nos. showed little decrease, but the Cu nos. increased very rapidly with increasing amts. of catalyst, showing that acetylation as well as acetylation had taken place. K. and K. have also made a critical study of methods for detg. the Ac content of cellulose acetates. Under properly standardized conditions, the alk. sapon. of the acetates is more satisfactory than the acid hydrolysis, which is tedious and gives no definite end point. The sample of acetate is allowed to swell in neutral 75% EtOH , and after cooling is treated with an excess of 0.5 *N* NaOH . After standing for 24 hours at room temp. (shaking at intervals) the excess of alkali is titrated, and the % Ac computed. The article is replete with well tabulated analytical data.

L. E. WISE

Hydrocellulose. EMIL HEUSER AND WALTER VON NEUENSTRIN. *Cellulosechemie*

3, 89-96, 101-7(1922).—Methylation of purified cotton cellulose gives good yields of dimethylcellulose. Only small amts. of water-sol. products were obtained. Denham's results on the formation of trimethylcellulose (*C. A.* 15, 1603) were not duplicated. Hydrocellulose prep'd. according to Knoevenagel and Busch (*C. A.* 16, 2779) is more readily methylated with NaOH and Me_2SO_4 than is cellulose itself and gives good yields of *dimethylhydrocellulose*, (A). K. and B.'s "hydrocellulose" may, therefore, be a chem. individual. A is very sol. in cold H_2O but is pptd. when the soln. is heated; it is sol. in CHCl_3 , $\text{CHCl}_3\text{-C}_2\text{H}_5\text{OH}$, AcOH , $\text{C}_6\text{H}_6\text{N}$, and is insol. in concd. NaOH. Whereas K. and B.'s hydrocellulose had a Cu no. of 7.9-8.7, A has no reducing action. Other methods of methylating hydrocellulose did not give uniform products, although the MeO content was higher than in A. "Girard's hydrocellulose" yielded a heterogeneous product on methylation which indicated that the original sample was a mixt. of unchanged cellulose and hydrolyzed material. Acetylation of A yielded 30% of a *compd.* (26% OCH_3 ; 17% Ac) having the approx. compn. of a *dimethylacetylcellulose* (B), m. (approx.) 110° , sol. in Et_2O but insol. in H_2O , and a *substance* (23% OCH_3 ; 17% Ac), m. 140° insol. in H_2O but sol. in Me_2CO . Small amts. of other substances also were formed. Mol. wt. detns. on A and B gave very variable results, so no conclusions can be drawn regarding the degree of polymerization of either of them. L. E. WISE

Chemical properties of pulps prepared by indirect cooking. M. W. BRAY AND T. M. ANDREWS. *Paper Trade J.* 76, No. 3, 49-52(1923).—With all conditions const. except time, a series of spruce sulfite pulps was prep'd. by indirect cooking. These pulps were compared with commercial pulps made under similar conditions. The basis of the comparison was the cellulose content; a high cellulose content appears to be necessary to produce a good pulp. The % of stable and unstable celluloses are also indications of the quality of pulp, the pulp with the greater amt. of stable (α) cellulose usually being of a superior quality. The pulp deteriorates with the overcooking necessary to remove all the lignin. Until the 9th hr. of cooking the cellulose and lignin content of the pulp are very nearly the same as those of wood. The 1st few hrs. of cooking does not affect the alkali-sol. material. In the latter part of the cook a larger amt. of this material is removed. While the character of the cellulose and the lignin content are indicative of the quality of the pulp produced, the other factors not well understood appear to exert considerable influence. Cellulose is always lost during the removal of the lignin, and it seems 45% is about the max. yield of cellulose by present commercial methods of sulfite cooking. C. J. WEST

Determination of the bleach requirements of pulp. BJARNE JOHNSEN AND J. L. PARSONS. *Zellstoff Papier* 2, 258-61(1922); *Pulp Paper Mag. Can.* 21, 53-5(1923).—The method depends upon the action of KMnO_4 upon unbleached pulp. Ten g. pulp is disintegrated in a total of 225 cc. H_2O , brought to 25° , 25 cc. $N \text{ KMnO}_4$ added and the mixt. is allowed to stand 1 hr. The mixt. is then filtered and 10 cc. of the filtrate poured into 10 cc. $0.1 N (\text{CO}_2\text{H})_2$ in 100 cc. H_2O and titrated with $0.1 N \text{ KMnO}_4$. The no. of cc. required for this titration is called the KMnO_4 no. For hard pulps only 5 g. of pulp may be used and the result multiplied by 2. Comparison is made with Sieber's Cl-consumption method; the 2 have about the same value. C. J. WEST

Sedimentation control of ground wood. W. A. MONROE. *Paper Trade J.* 74, No. 15, 235, 237; *Paper* 30, No. 7, 45-46, 48(1922).—The Ground Wood Committee, T.A.P.P.I., recommends 2-orifice type of freeness tester for ease and accuracy. Freeness of stock depends on wood, temp. and white-water. This varies almost directly as the temp., results being shown as a curve. Three tests are made on stock from service box of the paper machines, from the groundwood deckers and the sulfite deckers. Av. is accepted as accurate figure. Then a sample of stock is taken from each stone in the

grinder room. This enables better treatment of grinding stones and a more uniform stock. C. J. WEST

Sulfite alcohol. HENRI DU BOISTRESSELIN. *Mon. sci.* [5] 12, 97-105(1922).—A review. A. P.-C.

The chlorine processes for the manufacture of paper pulp. RAYMOND FOURNIER. *Papier* 25, 481-90(1922).—A review. A. P.-C.

Determination of the moisture content of paper pulp. RAYMOND FOURNIER. *Papier* 25, 520-4(1922).—F. suggests mixing a given wt. of the pulp with a given wt. of a soln. of known strength of a substance having no action on the pulp and detg. the content of the substance. A. P.-C.

Use of rubber in the manufacture of paper. RAYMOND FOURNIER. *Papier* 25, 544-7(1922).—Brief discussion of Kaye's patent (*C. A.* 16, 342). A. P.-C.

The manufacture of paper pulp in France and its colonies. A. R. DEVAINS. *Papier* 25, 337-47(1922); *Chimie et industrie* 8, 767-81(1922).—The sulfite, soda and sulfate, and CI processes for the manuf. of pulp are briefly described, and the French supplies of raw materials and the suitability of the various processes from the standpoint of obtaining a self-contained French industry are discussed. The soda and CI processes are the most suitable. With regard to colonial resources, apart from esparto, which can be transported economically from Northern Africa to France for the manuf. of pulp, *bamboo*, *papyrus*, "*ravenala*," and *rice straw* can be economically worked in the colonies. The most suitable process is the CI process, as the consumption of CI and of NaOH can be made proportional to the amts. in which they are produced in the electrolysis of NaCl and consequently no NaOH recovery is required. A. P.-C.

Colloidal rosin size. G. DEMARCANDIÈRE. *Papeterie* 44, 970(1922).—The colloidal size prep'd. by the Etablissements Gillet contains free rosin 12.46%, combined rosin 38.54, Na₂O 2.92, H₂O 46.08. It is fairly transparent but somewhat cloudy, is viscous, and dissolves in hot water to a pure white milk without leaving any residue. With Al₂(SO₄)₃ it gives a gelatinous, unctuous, and remarkably white ppt., which, differing from other Al⁺resinates, seems to become whiter when exposed to the action of air or sunlight. With CaO or CaSO₄ it gives gelatinous and unctuous ppts., while other sizes give ppts. like very fine white sand. Under the influence of even very moderate heat the Ca resinate obtained from colloidal size forms a very homogeneous lacquer (somewhat similar to an oil varnish) which ensures perfect sizing. A. P.-C.

Paper-making materials from India and Nigeria. ANON. *Bull. Imp. Inst.* 20, 287-92(1922).—*Talipot palm leaf stalks* from India contained H₂O 10.1, ash 4.7, cellulose (on stalks as received) 46.8, cellulose (on dry basis) 52.1%. The length of ultimate fibers was 0.7-2.7, mostly 1.0-2.0, av. 1.5 mm. The stalks when boiled 6 hrs. at 140° with 20% NaOH (on the wt. of stalks) as a 4% soln. gave 45.5% unbleached and 39% bleached pulp; the NaOH consumption was 13.9%. The pulp contained a small amt. of insufficiently disintegrated fibers and would not bleach satisfactorily. Increasing the temp. to 160° gave a pulp consisting of well sepd. fibers, having good felting power, which would not bleach readily with 24% of bleach. A fairly white pulp was obtained with 40% of bleach, yielding an opaque paper of good strength. The unbleached pulp yields a strong brown paper suitable as wrapping paper. *Betel nut husks* from India contained H₂O 10.5, ash 6.3, cellulose (on husks as received) 42.6, cellulose (on dry basis) 47.6%. Ultimate fiber length 0.3-1.4, av. 0.6 mm. When boiled for 6 hrs. at 160° with 18% of NaOH as 3% soln., 43% of unbleached pulp was obtained with a consumption of 10.4% NaOH. A small amt. of coarse fiber was unbroken, the paper obtained was of poor strength, and bleaching with 30% of bleach gave only a pale buff-colored

pulp. Treatment with 22% of NaOH as a 3.67% soln. gave slightly better results. The difficulty is due to the varying resistances of the different parts of the husks to the action of the NaOH, mild treatment having but little effect on the coarser fibers and drastic treatment injuring the finer ones. The paper is very weak owing to the extreme shortness of the fibers. *Elephant grass* (*Pennisetum purpureum*, Schumacher) from Nigeria contained H₂O 8.7, ash 2.9, cellulose (on grass as received) 54.0, cellulose (on dry basis) 59.1%. Ultimate fiber length 0.5-3.2, av. 1.4 mm. The grass, when boiled 5 hrs. at 160° with 16% of NaOH as a 4% soln. yielded 48.3% of unbleached pulp with 10.0% NaOH consumption, which consisted of well disintegrated fiber and which yielded a pale brown paper of good strength. It was readily bleached with a 45.7% yield (on the grass), and after beating was satisfactory in texture and felting quality and furnished satisfactory white paper. A. P.-C.

Relation of the water content of paper to the degree of beating. G. DALÉN. *Mitt. Materialprüfungsamt* 39, 282-3(1921).—The amt. of H₂O taken up by paper after beating for various periods of time was detd. at 53%, 65% and 100% humidity. In unbleached pulp, the increase, even at the lower humidities, is quite marked when the degree of beating is increased from 11 to 88° (Schopper-Riegler). The bleached pulp did not show a very noticeable increase under the same conditions. C. J. WEST

Effects of temperature and humidity on the dimensions of paper. H. S. DAVIS. *Paper* 31, No. 12, 7-8, 10(1923).—With const. relative humidity, the dimensions of papers are substantially the same even though the temp. varies. When the abs. humidity is decreased at a const. temp. the dimensions decrease and *vice versa*, but the abs. humidity alone without consideration of the temp. does not det. the dimensions of paper. The rate at which the paper changes its dimensions is dependent upon the rate of flow of the air over it. This rate is fairly rapid, being nearly complete in 5-10 min. The rates are increased with rise in temp. C. J. WEST

Normal papers, 1919-1921. W. HERZBERG. *Mitt. Materialprüfungsamt* 40, Nos. 1-2; *Wochbl. Papierfabr.* 53, 4456-8(1922).—Tabular summary of tests made during 1919-1921. C. J. WEST

Use of corn starch in the paper mill. HANS WREDE. *Papierfabr.* 20, 1429-33 (1922); *Paper Ind.* 4, 1368-71; *Paper* 31, No. 12, 11-14(1923).—General discussion of the use of starch in writing and in printing papers, as a filler and in surface sizings. C. J. WEST

Stability of paper colors to bleach (HOLMES) 25. Experiments with rubber, celluloid and hexalin (JONES) 30. Possibilities in rubber latex (HUNTER) 30. Ethylcellulose solution (U. S. pat. 1,437,792) 5. Cellulose ether composition for coating films (U. S. pat. 1,437,828) 5.

Cellulose and other carbohydrate ethers; artificial threads; films; varnishes; plastic masses. G. YOUNG. *Brit.* 184,825, Sept. 12, 1921. Alkyl ethers of cellulose, starch, dextrin, and other carbohydrates of the general formula (C₆H₁₀O₄)_n, which are characterized by their insoly. in alc., benzene, and H₂O, are obtained by treating the carbohydrates with alkyl chlorides at a temp. of 100-150°, in the presence of caustic alkali or other metallic hydroxide together with an amt. of H₂O not greater than half the wt. of the alkali; it is preferred not to employ an excess of alkali, but an excess of alkyl chloride is used, preferably in the ratio of 20 mol. wts. of the chloride to 1 mol. wt. of the carbohydrate, taken as C₆H₁₀O₄—the excess of alkyl chloride is eventually recovered, as by

distn. The reaction is facilitated by the addn. of finely divided Cu or other catalyst, and an inert org. diluent such as benzene may be added. In working the process, cellulose is soaked in 40% caustic alkali soln., and afterwards pressed to give a product contg. 2 parts of cellulose, 2-3 parts of caustic alkali, and $1-1\frac{1}{2}$ parts of H_2O ; alternatively, the ingredients in these proportions may be ground or mixed together; the etherification is carried out in one stage and usually in an autoclave, and in the case of Et and Me chlorides at a temp. of 100° but a higher temp., preferably not exceeding 130° , is necessary with propyl, butyl, and amyl chlorides, etc.; during etherification, the reacting materials are preferably stirred or agitated. The ether is washed with H_2O , and is purified by soln. in glacial HOAc with subsequent pptn. with H_2O . Mixed ethers are obtained by employing a mixt. of alkyl chlorides. The ethers may be employed in the manuf. of artificial threads, films, varnishes, plastic masses, etc.

Cellulose nitrate solutions. J. C. CLANCY. U. S. 1,439,293, Dec. 19. Cellulose nitrate is dissolved in anhyd. NH_3 and the soln. thus obtained is used to transfer the nitrate to another solvent which may be less active alone, *e. g.*, mixts. contg. an alc. or ester and a chlorinated hydrocarbon.

Cellulose ethers. P. C. SEBL. U. S. 1,437,820, Dec. 5. A mixt. contg. cellulose and alkali is reacted upon by an etherifying agent, *e. g.*, $EtCl$, in contact with a steel autoclave lining which has been immunized against discoloration of the product by previous repeated treatment with the reagents used. U. S. 1,437,821 specifies gradually heating a mixt. of cellulosic material, alkali and etherifying reagent, *e. g.*, cellulose, H_2O , NaOH and $EtCl$, to a reaction temp., *e. g.*, $90-170^\circ$, and maintaining the mass at reacting temp. during further etherification.

Reducing shrinkage of cellulose ether films. N. S. KOCHER. U. S. 1,437,810, Dec. 5. Films mainly formed of cellulose ethyl ether are treated with H_2O at a temp. of about $0-10^\circ$ in order to effect preshrinkage.

Drying sulfite waste liquor. C. ELLIS. Can. 226,306, Nov. 21, 1922. A current of gas contg. some free O but less than does ordinary air is circulated and finely divided liquid to be dried is sprayed into the gas current in its circuit. The moisture is removed from the circulating gases at another portion of its circuit.

Pyroxylin composition. A. A. BACKHAUS. U. S. 1,437,952, Dec. 5. A plastic compn. adapted for the same uses as celluloid is prepd. by adding to pyroxylin a soln. of Et acetoacetate and $AcOEt$.

24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Estimation of the proportions of TNT and tetryl from the freezing point curve. C. A. TAYLOR AND W. H. RINKENBACH. *Ind. Eng. Chem.* 15, 73-4(1923).—As no satisfactory method existed for detg. the proportions in which TNT and tetryl exist in the mixts. of them found in detonators and detonating fuse the equil. temps. of known mixts. of these substances were studied by the methods described by Bell and his pupils (*C. A.* 14, 174, 347). When the time rate of cooling is plotted on a large scale the C' point can be checked to 0.2° and detd. in the curve to 0.2%. The C' point does not appear in mixts. contg. 55-65% of TNT but it may be developed and detd. with a fair degree of accuracy by adding to a known wt. of the mixt. a known wt. of TNT or tetryl, and a formula for calcg. from these data the % of component TNT in the mixt. is given. When the C' point obtained is between 67.5° and 80.3° to ascertain whether the point

is on the TNT or the tetryl side of the curve a quantity of the latter is added and another point on the curve is located while noting whether the temp. is higher or lower than the original temp. During this study the existence of the new *mol. complex* $2C_6H_5N_3O_6 \cdot C_7H_5N_3O_6$ was observed.

CHARLES E. MUNROE

The solubility of trinitrotoluene in organic solvents. C. A. TAYLOR AND WM. H. RINKENBACH. *J. Am. Chem. Soc.* 45, 44-59(1923).—Detns. were made of the soly. in water, Et_2O , $EtOH$, CS_2 , CCl_4 , $CHCl_3$, C_6H_6 , C_7H_8 , Me_2CO , $PhNH_2$ and C_6H_5N . With the first 5 solvents of low soly. a wagon *pipet* of special design was used and the ordinary procedure followed; with the last 6 of high soly. the cooling-curve method as developed by Bell and Hertzy was used. Me_2CO was the most active solvent, dissolving 57 g. of TNT at 0° and 2678 g. at 75° per 100 g. of Me_2CO . The known complex TNT- $PhNH_2$, m. $83-4^\circ$, was observed and a new *complex* TNT- C_6H_5N , m. $40-2^\circ$, was discovered. It could be formed by contact of the 2 substances without soln.

CHARLES E. MUNROE

The solubility of trinitrophenylmethylnitramine (tetryl) in organic solvents. C. A. TAYLOR AND WM. H. RINKENBACH. *J. Am. Chem. Soc.* 45, 104-7(1923).—Detns. by the wagon *pipet* were made for water, 95% $EtOH$, Et_2O , $CHCl_3$, CCl_4 and CS_2 , the soly. being comparatively slight in all cases and, in general, less than that for TNT in the same solvent under the same conditions. 95% $EtOH$ showed the greatest solvent power; 0.32 g. of tetryl at 0° and 5.33 g. at 75° were dissolved per 100 g. of solvent. C. E. M.

Sympathetic detonation tests of high-explosive shell. ANON. *Army Ordnance* 3, 180-2(1922).—It having become necessary to provide permanent storage for the large quantity of loaded H. E. projectiles remaining from the war supplies it developed there was little or no precise information as to the distances piles of a given caliber contg. known wts. of an explosive, such as TNT, should be sepd. from other piles of ammunition to prevent the explosion of the primary pile being communicated to the secondary ones. Hence as there is at hand considerable H. E. ammunition condemned for mech. defects but otherwise suitable for such tests a series of large-scale expts. is being carried out at Aberdeen in which a large central pile of shell is surrounded by other piles of shell sepd. from the central pile by known intervals and, in instances, by barricades such as might be conveniently erected in magazines. Diagrams and photographs indicate the method of procedure and many of the effects of these explosions in which as many as 1248 projectiles contg. some 40,584 lbs. of H. E. were used in a single test. With 384 shell in the central pile it was found that one shell detonating with high order will set off the whole pile and that when piled in standard magazine piles the secondary piles were exploded at distances of 200 in., and perhaps greater, from the primary pile, but that a barricade of 75-mm. shell boxes reduced the distance to 60 in. Burning of a carload of 200 8-in. shell contg. 80/20 amatol showed there would always be danger of complete detonation of the cargo under these circumstances. From the burning of a pile of 512 boxes of complete rounds of 75-mm. ammunition, it was concluded that detonations started in one box would not communicate to another box and this was supported by the results obtained when detonation was effected in one box of a pile of 49, though the entire contents of the primary box detonated. In the detonation of any considerable quantity of H. E. shell, such as a whole magazine pile of 400 or more, whole shell or fragments may be thrown a distance of 2 miles. CHARLES E. MUNROE

Colloiding agents for nitrocellulose. T. L. DAVIS. *Ing. Eng. Chem.* 14, 1140-41(1922).—Certain nonvolatile or high-boiling substituted ureas, urethans and sebacic, carbamic and phthalic esters having been used in colloiding nitrocellulose and coating grains of smokeless powder to reduce their hygroscopicity as well as impart other desirable properties a study has been made of their behavior in alc., C_6H_6 and ligroin solns.

It was found that the amt. of the agent necessary for complete gelatinization of pyrocellulose is greater in alc. than in C_6H_6 , and less than in ligroin. Alkylated ureas with but one alkyl or 2 unsym. alkyl groups appear to be without action on pyrocellulose but with 2 sym. alkyl groups they are excellent solvents and even when substituted by other aliphatic or aromatic groups; the heavier the alkyl group the greater is the gelatinizing power. Aromatic substituted ureas contg. less than 3 aromatic groups appear without action. The heavier the alkyl group in esters of sebacic and phthalic acids the more efficient is the action. Alkyl esters of aliphatic and aromatic substituted carbamic acid are excellent solvents but the aromatic appear without action when there are less than 3 aromatic groups present.

CHARLES E. MUNROE

Practical manufacture and use of liquid oxygen explosive for breaking ore. A. D. AKIN. *Eng. Mining J.-Press* 114, 978-80(1922).—A detailed account of operations at the Real del Monte Co.'s silver mine, Pachuca, Mex. Liquid O, of 95% O content, is made by the Linde method at the rate of 432 kg. per 8-hr. shift. The absorbent and combustible in the cartridges is lampblack made by combustion of *chapopote*, the residual gum of petroleum found in the crude state in Mexican oil fields. The explosive is styled LOX and it is fired by No. 8 detonators. Although the cartridges remain active for but 20 min. yet this company loads and fires a round of 25 holes without undue haste. A 227-g. LOX cartridge contg. 65 g. C and 162 g. O is found equal in efficiency to 250 g. of 40% gelatin dynamite and, per ton of rock broken, costs 80% as much. At the Rosario mine 90% of the 12,000 tons broken down per month is broken by LOX, it being used where there is ease of access to the face. With it there are no noxious gases, no danger in mucking out from unexploded charges and absolute safety from mis-fires after 20 mins. The LOX cartridges are 1.38 x 12 in., while the gelatin dynamite are 1.25 x 8 in.

CHARLES E. MUNROE

Coal dust explosion tests in the experimental mine 1913 to 1918 inclusive. G. S. RICE, L. M. JONES, W. L. ERGY AND H. F. GREENWALD. Bur. of Mines, *Bull.* 167, 639 pp., 62 tables, 31 plates, 82 figs.(1922).—Many important conclusions were drawn regarding the way a coal-dust explosion may originate, the mechanism of an explosion, and the methods of preventing and of limiting explosions.

C. E. M.

Explosions of gaseous mixtures. A. P. KRATZ AND C. Z. ROSENCRANS. Univ. Ill. Eng. Expt. Sta., *Bull.* 133, 96 pp.(1922).—This report covers the results of a study of the physical phenomena involved in the explosions of various mixts. of illuminating gas and air, with respect to the effect of shape of the explosion vessel and of turbulence at the time of ignition. Heat losses also were measured. For the gas used (compn. not given) the air-gas ratio 4:1 gave the max. explosion pressure and the min. explosion time, results which were still further accentuated by the mixing effects produced by turbulence. The position of the source of ignition in the vessel affects the rate of explosion and the max. pressure; the most favorable location is the center of the head. A spherical vessel gives the best results, with conical and cylindrical next in order and the L-head type last with results 16.5% lower than the first. The rate of gas cooling after the attainment of max. pressure varies directly with the ratio of surface to vol. of the explosion vessel.

H. L. OLIN

New invention eliminates accidental explosion in gas mixtures. H. C. P. WEBER. *Chem. Met. Eng.* 27, 942-3(1922).—The essential feature of the device is the application of a catalyst to a considerable porous surface and the control of the resistance of the system so that the combustible component of an explosive gaseous mixt. will be oxidized at a temp. considerably below the explosion point of the mixt., the object sought being to eliminate the danger of explosion of explosive mixts. in mines, submarines and elsewhere, by continuously destroying the mixt. The device exhibited takes the form

of a Pt spiral enclosed in a fine wire screen and attached to a lamp base of the ordinary type fitting the ordinary socket of a 110-v. circuit. The temp. used differs with the catalyst. With Pt a temp. of 600-800° was found most satisfactory. Data are given for expts. with bare wire, wire + various catalysts and for different gas mixts. The device functions even in H + air mixts. contg. 10-15% of H. CHARLES E. MUNROE

Fire and explosion hazards of petroleum and petroleum products. S. H. KATZ AND N. A. C. SMITH. Bur. of Mines, *Repts. of Investigations* No. 2400, 11 pp. (1922).—Reviews the special hazards which menace crude and refined oils in production, storage, refining, distribution and use growing out of the association of petroleum with inflammable gases and the fact that it contains or yields various percentages of readily volatile and easily ignitable hydrocarbons. Graphs showing temp.-pressure relations of petroleum products and H₂O at high temps.; typical distn. curves of petroleum products; and results of vapor-pressure detns. with 5 different grades of gasoline together with tables of flash points of representative petroleum and its products, and of some dye intermediates are given. Many other useful data are assembled and it is concluded that "to translate the above facts into safety measures requires that all hot objects or sources of heat whatsoever should be kept away from petroleum, petroleum products, and similar flammable liquids." CHARLES E. MUNROE

Mineral fires in the Huelva Pyrites Mines, Spain. A. O. BROWN. *Iron Coal Trades Rev.* 105, 737 (1922).—The ore mined is mainly an intimate mixt. of FeS₂ and chalcopyrite (Cu₂S·FeS₂). The Cu content averages about 1.5%, S 45-47, Fe 40, small amts. of Zn, As, Pb, etc. with 5-10% of insol. Al₂O₃·2SiO₂. Cu also occurs in the zones of secondary enrichment as chalcocite (Cu₂S). There are zones, chiefly in depth, where there is a greater development of Cu₂S·FeS₂ often accompanied by blende and galena. The ore extends to depths of 330 to 1640 ft. Spontaneous combustion caused by oxidation in fallen masses of ore is the probable cause of mine fires. It is more prevalent in the zones containing Cu₂S. Heat generated by a fall or movement of mineral will not of itself cause a fire; it only assists by exposing larger surfaces to oxidation. Fires are rarely completely extinguished. Flooding with water or cooling by large vols. of low-pressure air are the methods usually employed until the area can be worked out. Details of their application are given. J. L. WILEY

PRICE, DAVID J. AND BROWN, HAROLD H.: **Dust Explosions.** Boston: National Fire Protection Association. 246 pp. Reviewed in *J. Western Soc. Eng.* 27, 177 (1922).

Smokeless powder. T. L. DAVIS. U. S. 1,439,505, Dec. 19. A smokeless powder is formed of nitrocellulose and diphenylpyrazolone or phenylmethenylpyrazolone or a similar substituted pyrazolone or pyrazolidone. Cf. C. A. 17, 472.

Modifying viscosity of smokeless powder. R. G. WOODBRIDGE. U. S. 1,439,656, Dec. '19. The viscosity of smokeless powder contg. diphenylamine is reduced by heating the powder to about 75-135° while immersed in an org. liquid in which the powder is substantially insol., e. g., EtOH. The process is adapted for reworking "pyro" powder for general industrial purposes.

Slow-burning black powder explosive. J. P. GRAY. U. S. 1,438,759, Dec. 12. About 2-12% of rosin is incorporated in explosives of the black-powder type, contg. nitrate, S and charcoal, to reduce the burning speed.

Blasting detonator. W. Eschbach. U. S. 1,438,431, Dec. 12. Detonators are formed with an Al shell and a filling of Pb azide or a Pb azide mixt. and similar detonat-

ing compns. which are inert to Al and which can be easily clipped on to a quick-match by clamping tongs.

Composition for detonators. B. GROTTA. U. S. 1,439,009, Dec. 19. Detonators are charged with a mixt. of mercurous azide, Hg fulminate, KClO_3 and TNT, which is unimpaired by pressures at which Hg fulminate or its mixts. with KClO_3 become "dead-pressed."

Filling explosive shells. C. W. PORTER. U. S. 1,438,399, Dec. 12. Explosive shells are filled with CO_2 or N or other inert gas prior to introduction of the explosive, to lessen danger of accidental explosion.

Explosive shell charged with liquid oxygen or air and carbonaceous material. P. HRYLANDT. U. S. 1,439,237, Dec. 19.

Cup for explosive primers. J. M. OLIN. U. S. 1,438,779, Dec. 12.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

A history of the chemistry of the more important natural dyes. EMIL LESSER. *Am. Dyestuff Rep.* 12, 1-4(1923). E. J. C.

Review of the British dyestuff industry in 1922. WM. ALEXANDER. *Chem. Age* (London) 7, 919-20(1922). E. J. C.

Colloidal chemistry and dyeing. R. HALLER. *Kolloid-Z.* 31, 295-9(1922).—A review. A. MUTSCHALLER

The acylaminoanthraquinones as vat dyes. E. GRANDMOUGIN. *Compt. rend.* 175, 970-3(1922).—An account of the various tints, and the varying degrees of affinity for vegetable fiber, manifested by the acylaminoanthraquinones as vat dyes. I. P. ROLF

The manufacture of malachite green. J. R. MINEVITCH. *Color Trade J.* 11, 233-7(1922); cf. *C. A.* 16, 2994.—A discussion of research which shows that the usual oxidation of tetramethyldiaminotriphenylmethane by PbO_2 in a soln. contg. HCl or mixt. of HCl and AcOH gives a mixt. of carbinols in definite proportion. One of these, tetramethylcarbinol, is cryst. and produces cryst. malachite green salts while the others are noncryst. and give amorphous salts. Expts. show that mineral acids favor the formation of the noncryst. carbinols and org. acids favor the production of the cryst. carbinol. In oxidizing, sufficient mineral acid to bring the leuco base into soln. and react with the PbO_2 is necessary, as the base is almost insol. in AcOH, but the AcOH does keep the liberated carbinols in soln. The max. yield of cryst. malachite green salts is obtained by oxidation in a soln. contg. 2.44 mols. HCl and 2.20 mols. AcOH at temps. below 21° . By adding extra mol. proportions of HCl simultaneously with the PbO_2 during the oxidation the pptn. of the leuco base from the soln. due to decreased mineral acidity is avoided and the yield of cryst. carbinol is theoretical. CHAS. E. MULLIN

The dangers of the titanium chloride method for determining the strength of dyes. E. H. GAMBLE AND R. E. ROSE. *Color Trade J.* 11, 238-9(1922).—Practical application of the TiCl_3 titration method of evaluating dyestuffs shows that it is not suitable for comparing dyes of different manuf. as even slight differences in the method of manuf. may show wide apparent differences in value although the dyeing test may prove them to be identical in value. It is recommended as an excellent check upon standardization and uniformity by manufacturers upon their own product. CHAS. E. MULLIN

Coloring matter of the fruit of *Gardenia florida* L. T. MUNESADA. *J. Pharm.*

Soc. Japan No. 486, 666-71(1922).—This coloring matter has long been used as a dye in Japan (German "Gelbschote"). Rochleder and Mayer found that the coloring matter of *Gardenia grandiflora* Lou belongs to the safran group; this was named crocin, and on hydrolysis yields a sugar and crocetin. Since some botanists believe *grandiflora* and *florida* are the same plant, or at least very similar species, M. first attempted to identify safran in the latter. On extrn. of this fruit with H_2O , a sirupy coloring matter was obtained which on hydrolysis gave a H_2O -insol. substance which could not be crystd. out. Various salts, however, could be obtained in cryst. form. K salt, $C_{10}H_{13}O_7K$, gave orange-yellow crystals which changed to a red powder on heating at $270-90^\circ$; Na salt, $C_{10}H_{13}O_7Na$, short, yellow needles; and NH_4 salt, $C_{10}H_{13}O_7NH_4$, red-yellow needles. The original compd. thus corresponds to $C_{10}H_{13}O_7OH$, crocetin, obtained by Decker by hydrolysis of safran. Therefore, the coloring matter of the fruit of *Gardenia florida* L. contains safran. Further studies on the nature of its derivs. are now in progress.

S. T.

The relative stability of paper colors to bleach. W. C. HOLMES. *Color Trade J.* 11, 255-6(1922).—About 80 paper dyes and pigments are classified according to their fastness on bleached sulfite pulp to 0.05, 0.1, 0.17, 0.28 and 1.4% available Cl as $Ca(ClO)_2$. The light-fastness of dyestuffs cannot be accepted as an indication of fastness to bleach, as suggested by Bancroft.

CHAS. E. MULLIN

Progress in the field of artificial silk. K. SÜVERN. *Z. angew. Chem.* 36, 21-1 (1923).

E. H.

A troublesome defect in silk goods. JAMES CHITTICK. *Textile World* 62, 2921-3 (1922).—In satins of heavy construction a grayish dust or an accentuated "lousiness" sometimes appears in a very intermittent way. Microscopic examn. shows this to be caused by a kind of dirty, greasy, gray substance like lint, composed of fiber and dirt held together by a slight oiliness. A thorough cleaning of the machinery obviates the trouble.

CHAS. E. MULLIN

Value of the serigraph test. W. F. EDWARDS. *Textile World* 62, 3569-73, 3681-5, 3689(1922).—After extensive expts. the United States Testing Co. concludes that for the strength, elasticity and elongation tests of raw silk the serigraph is consistent and reliable. Three charts and 9 tables of results are given.

CHAS. E. MULLIN

Recent progress in solvent scouring of fibrous materials. H. HEY. *J. Soc. Dyers & Colourists* 37, 183-7(1921).—The article is supplementary to the lectures given in 1919 and 1920 (cf. *C. A.* 13, 662; 14, 1444; 15, 1405). Solvent scouring is suggested for piece goods. Gasoline as solvent is recommended, with the addn. of oleate soaps. The soly. of Ca and Mg soaps in the solvent make the process particularly adapted to the scouring of lime-slipd wools. These metallic soaps aid in cleansing and emulsify the moisture and dirt contained in the stock. Solvent contg. emulsified water is difficult to filter but may be clarified centrifugally. Static elec. charges are avoided by the presence of Mg oleates, free fatty acids or alc., which render the solvent a conductor. About 14 gal. of solvent are lost per 1000 lbs. of wool scoured.

CHAS. E. MULLIN

The solvent scouring of hosiery wools, yarns, and knitted goods. H. HEY. *J. Soc. Dyers & Colourists* 37, 81-2(1922); cf. preceding abstr.—With this process felting and shrinking are eliminated. It is also particularly suitable for the finer and long staple raw wools. The most recent type of machine is continuous, the material passing through in a thin layer. It is first showered with solvent to remove the grease and dirt, later it is sprayed with water to remove any remaining dirt, and is then dried by warm air. Wool carbonized in the grease by the acid process and then solvent scoured before washing is cleaner and better than stock scoured before carbonizing. The de-

teriation of fine colonial scoured wools during storage and transportation is discussed.

CHAS. E. MULLIN

Cotton softeners. P. F. ESREY. *Am. Dyestuff Rept.* 11, 299-300(1922).—In the recipes given, unless otherwise stated the fats and oils are mixed and melted, the lye is brought to a boil in a sep. container and the melted fats are poured into the boiling lye, boiled a few min. with const. stirring and allowed to cool. Only a portion of the fats should be saponified as the uncombined fatty matter is the most important factor for softening and readily emulsifies with the soap formed. The following recipes are given: stearic acid 1 lb., 25% ammonia 0.4 lb., water 2 lbs. Mix the water and ammonia, heat and add the melted stearic acid. *Castor-paraffin softener:* paraffin wax 49 g., castor oil 81, stearic acid 78, NaOH 75°Tw. 20 cc., water 600 cc. *Tallow-coconut oil-oleic acid softener:* oleic acid 1275 g., tallow 1000, coconut oil 618, NaOH 68° Tw. 116 cc., water 5 l. A sol. oil-base softener may be made by boiling slowly for 1 hr. 100 gal. of sol. castor oil with 25 gal. of light colored mineral oil, stirring meanwhile with a mech. agitator. Allow to cool overnight. A heavy finishing oil may be made from sol. castor oil 5000 cc., light mineral oil 480, cylinder oil 300, tallow 290 g., vaseline 300 g., NaOH 72° Tw. 175 cc. water 2000 cc.

L. W. RIGGS

Electrochemical mercerizing. RAFFAËLE SANSOME. *Textile World* 62, 2469-71, 3013-4(1922).—After a general discussion of mercerizing and *recovery of soda*, it is suggested to recover the soda by treating the mercerized cloth with CO₂ in a special gassing chamber and then merely rinsing, instead of the usual acid treatment. C. E. M.

Scheme for estimating the washing and cleansing actions of detergents. P. HEERMANN. *Mitt. Materialprüfungsamt* 39, 65-72(1921); cf. C. A. 15, 2993. **Technical economy of raw material in textile administration.** *Ibid* 72-5.—Losses in the operations of the textile industry are pointed out and suggestions given for their avoidance. **Spotting and tendering of textiles in consequence of defects in carbonization.** *Ibid* 75-8; cf. C. A. 15, 3753. **Permanent chlorine bleaches and their influence on the durability of cotton.** P. HEERMANN AND H. FREDERKING. *Ibid* 131-9; cf. C. A. 12, 1254, 2448; 13, 1404, 1539; 15, 2993; 16, 2415, 2416.

L. W. RIGGS

Humidity in woolen and worsted mills. A. W. THOMPSON. *Textile World* 62, 2893, 2907-13, 3185-6, 3199-3203, 3315-7(1922).—A discussion of the importance of proper humidity in carding, spinning and weaving woolens, and in carding, combing, spinning and weaving worsteds by both the Bradford and French systems. C. E. M.

Possibilities in rubber latex (HUNTER) 30. Artificial daylight (for color matching) (LAMPLUGH) 2. Filaments from basalt (U. S. pat. 1,438,428) 18.

Color Index. Part I. Synthetic Organic Dyestuffs. Edited by DR. F. M. ROWE. Bradford, England: Society of Dyers and Colourists. 24 pp. Reviewed in *J. Textile Inst.* 13, 184(1922).

Dyes. DURAND ET HUGUENIN SOC. ANON. *Brit.* 165,721, June 14, 1921. Halogenated acridine dyes are obtained by halogenating basic acridine dyes or their leuco compds., preferably in the presence of a solvent or diluent. They dye leather, tannin-mordanted cotton, and natural or artificial silk, red-orange to red shades fast to Cl and redder than those yielded by the parent dyes. In examples, (1) acridine orange is added together with NaBr to H₂SO₄, the mixt. heated, poured on to ice and the dyestuff

salted out; (2) acridine orange is treated with Br and NaClO₂ or Br alone, in nitrobenzene soln. Other examples are cited.

Dyes. DURAND ET HUGUENIN SOC. ANON. Brit. 166,530, July 11, 1921. Triarylmethane dyes, dyeing chromed wool, are obtained by oxidizing a mixt. of a methylenedianilino-*o*-hydroxyarylarboxylic acid with an *o*-hydroxyarylarboxylic acid, or their substitution products. In the prepn. of the methylenedianilino-*o*-hydroxyarylarboxylic acids, either an anilino-*o*-hydroxyarylarboxylic acid may be condensed with HCHO or the *o*-hydroxyarylarboxylic acid may be condensed with HCHO and then the anilino group introduced. Examples are given.

Dyes. SOC. ANON. POUR L'INDUSTRIE CHIMIQUE À BÂLE and F. STRAUB. Brit. 186,635, March 18, 1921. Addition to 104,045 (C. A. 11, 2046). The Cr compds. of chromable azo dyes described in the principal patent are prepd. by treating the dyestuffs in question in alk. soln. with the complex Cr compds. made by action of alk. suspensions of Cr hydroxide on org. compds. contg. more than 1 hydroxyl group. The process permits the use of Fe vessels. *E. g.*, the dyestuff from diazotized 1-hydroxy-2-amino-4-chloro-6-benzenesulfonic acid and 1-phenyl-3-methyl-5-pyrazolone is boiled with the Cr compd. from gallic acid or glucose, the free alkali neutralized and the Cr compd. are salted out. The products dye wool blue, violet or red shades fast to light and fulling. Complex Cr compds. of org. compds. are obtained by heating the parent compds. with alk. suspensions of Cr hydroxide, *e. g.*, polyhydric alcs. and phenols, tanning agents, sugars, degradation products of cellulose, and waste products from sulfite cellulose manuf.; glycerol, glycol, glucose, tannin, gallic acid and phloroglucinol are mentioned. The compds. may in part be sepd. from their aq. solns. by evapn. or by salting out.

Dyes for calico printing. C. JÄGERSPACHER. U. S. 1,437,758, Dec. 5. Monoazo dyes are formed from 1-amino-2-hydroxynaphthalene-4-sulfonic acid and resorcylic acid. The dyes thus formed are dark powders, sol. in Na₂CO₃ soln. and in concd. H₂SO₄ with a violet-red to violet color and yielding on cotton, when printed with Cr salts, violet-blue to violet-brown colors fast to soaping and to light.

Dyes from anthraquinone derivatives. B. MAYER, W. MOSER and J. WÜGLER. U. S. 1,436,770, Nov. 28. Successive condensation of β -naphthoquinone-4-sulfonic acid with equi-mol. proportions of α -aminoanthraquinone and 1,2-diaminoanthraquinone yields a dye giving bluish Bordeaux tints on cotton. By substituting 1-amino-4-methoxyanthraquinone for the second component a violet is obtained on cotton. Bordeaux tints are obtained when 1-amino-8-chloroanthraquinone is used as the second component with 2,3-diaminoanthraquinone as third component and with the same substitution, of the third component only, a heliotrope dye results. Dyes of various shades of red or bluish Bordeaux are prepd. from 6-bromo- β -naphthoquinone (or β -naphthoquinone-4-sulfonic acid, 2 mol. or 3-bromo- β -naphthoquinone, 2 mol.) combined with α -aminoanthraquinone (or 1,5-diaminoanthraquinone) and then with 2,3 (or 1,2 or 2,3)-diaminoanthraquinone. The dyes are used in alk. hyposulfite vats.

Modifying mercerized cotton fabric with nitric acid or zinc chloride. GEORGES HEBERLEIN. U. S. 1,439,515, Dec. 19. A permanent wool-like effect is produced on cotton fabric by first mercerizing it and then treating it with 43–46° Bé. HNO₃, and washing. U. S. 1,439,516 specifies the use of a 66° Bé. soln. of ZnCl₂ instead of the HNO₃ soln. after mercerization.

Modified mercerized cotton fabric. G. HEBERLEIN. U. S. 1,439,520, Dec. 19. After mercerization, cotton fabric is treated with 1.19 sp. gr. HCl at a temp. below 0° and washed, to produce a wool-like effect. U. S. 1,439,521 specifies the use of Schweizer's soln. instead of HCl, in an otherwise similar process.

Rendering cotton fabric transparent. G. HEBERLEIN. U. S. 1,439,512, Dec. 19. Transparent "all over" effects on cotton fabric are produced by successive treatment of the fabric with a soln. of NaOH and a 51-54° Bé. soln. of H_2SO_4 , followed by washing.

Wool-like effect on cotton fabrics. G. HEBERLEIN. U. S. 1,439,513, Dec. 19. Cotton fabrics are treated with H_2SO_4 of 49-51° Bé., washed and then treated with a soln. of NaOH without stretching, to produce wool-like effects. U. S. 1,439,514 specifies the production of wool-like effects on cotton fabrics by treatment with a mercerizing NaOH soln., then with 55-57° Bé. H_3PO_4 , and washing.

Wool-like effect on cotton fabric. GEORGES HEBERLEIN. U. S. 1,439,518, Dec. 19. Cotton fabric is treated with a cellulose-solubilizing salt such as ZnCl_2 or Schweizer's soln. to alter the fiber so that when it is afterward treated with a soln. of NaOH without stretching it is given a wool-like quality.

Linen-like effects on cotton fabrics. EDUARD HEBERLEIN. U. S. 1,439,519, Dec. 19. Cotton goods, the threads of which do not exceed the fineness of English yarn No. 80, are treated with a NaOH soln. of at least 15° Bé. at a temp. of about -5° or lower and afterward subjected to the action of 51-54° Bé. H_2SO_4 at a similar low temp.

Transparent lustrous effects on thin cotton goods. EDUARD HEBERLEIN. U. S. 1,439,517, Dec. 19. Yarn or thin cotton fabric is alternately treated with NaOH soln. of 15° Bé. or stronger at temps. below 0° and with H_2SO_4 of about 51-55° Bé.

Drying artificial silk. E. BRONNERT. U. S. 1,437,491, Dec. 5. Freshly pptd. somewhat gelatinous cellulose hydrate which may be in the form of filaments is subjected to the action of a continuously moving strong current of air of a temp. of 100-140°, the flow of which is regulated so as to maintain a uniform temp. at each cross-sectional portion of the drying chamber.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Titanium colors. HJALMAR OLSEN. *Edel-Erden u. Erze* 4, 1-3(1923).—Pure TiO_2 , and its hydrates and basic sulfates are used as a white pigment. "Titanium-white" is principally c. p. TiO_2 (65-90%); the composition-titanium pigment contains 25-35% TiO_2 pptd. on a suitable base. The methods of prep. these pigments from rutile and ilmenite are given. They have a sp. gr. of 4.0-4.3; the n of titanium-white is 2.60 (lead-white 1.99, zinc-white 1.90) and of linseed oil 1.49. The large difference in indices of oil and pigment give the paint high covering power. The paint is almost unaffected by weather and acid vapors or gases. It is inactive with oils, varnishes and lac.

EDW. F. HOLDEN

United States Government specification for turpentine. (Gum spirits and wood turpentine.) Federal Specification Board, *Standard Spec. No. 7; Circ. of Bur. of Standards No. 86*, 11 pp.(1922).

E. J. C.

Extraction and its application. II. Rosin and turpentine oil. J. MERZ. *Z. deut. Oel-Fell-Ind.* 42, 773-4(1922); cf. C. A. 16, 3988.—While most European countries still use the primitive method of destructive distn. to obtain the resinous products from the stumps of pines and similar needle trees, Czecho-Slovakia, Poland and several other small states, have developed the extn. method with solvents (benzine, benzene, trichloroethylene, turpentine, etc.) and obtain water-white oil of turpentine and high-grade rosin, and extd. wood fiber, suitable for cardboard, as a by-product. A brief description is given of the construction and operation of the app., which consists of a

steam-coiled extractor, contg. the disintegrated wood, with a cooling coil below its head, so as to condense the solvent-vapors sufficiently to drip back upon the charge, and a condenser whose inlet valve is opened when the extrn. is complete (8-9 hrs.). The condenser is mounted above the extractor so as to fill the latter by gravity with fresh solvent for the next charge. P. ESCHER

Recent research on formaldehyde resins. A. A. DRUMMOND. *J. Soc. Chem. Ind.* 41, 522-3R(1922).—A review. E. J. C.

The differentiation of the liquid resins of *Juniperus oxycedrus* and *Cedrus atlantica*. R. MASSY. *Bull. sci. pharmacol.* 29, 622-5(1922).—By fractional distn. in steam of the alkalized fluid resins, it is possible to differentiate the products. *Juniperus oxycedrus* yields fractions showing rotation from -5.4 to -12.6° . *Cedrus atlantica* gives fractions which have the values $+23.6^\circ$ to $+43.3^\circ$. F. S. HAMMETT

The crystalline constituents of the resins of conifers. A. DUFFOUR. *Bull. sci. pharmacol.* 29, 641-4(1922).—A review. F. S. HAMMETT

Sangajol (JUNGKUNZ) 22.

Paint containing zinc. H. N. COPTHORNE. U. S. 1,439,610, Dec. 19. A heat-resisting paint adapted for use on steel smoke stacks is formed of Zn dust 60, pine tar 5, carnauba wax 5 and a volatile solvent such as turpentine and naphtha about 30 parts.

Cold-water paint. F. BELL. U. S. 1,438,627, Dec. 12. A cold-water paint is prepd. by mixing an aq. glue soln., clay, whiting, ultramarine, lysol or other antiseptic and NaOH and a dye, draining off surplus H_2O and forming the material into cakes.

Titanium oxide pigment. W. F. WASHBURN. Can. 225,981, Nov. 14, 1922. A pigment contg. cryst. TiO_2 and combined P is prepd. by mixing a compd. comprising essentially TiO_2 with a compd. of P and calcining the mixt. at a temp. below its m. p. Cf. C. A. 16, 2035.

Embossed printing. D. G. EISEN. U. S. 1,438,815, Dec. 12. An ink which is adapted to be liquefied by heating is applied to paper or other fabric and the material is afterward subjected to pressure of a heated embossing device to form raised characters which may simulate embroidery.

Ink. A. B. DICK and E. W. HILL. U. S. 1,439,356, Dec. 19. An ink for use on rotary stencil duplicating machines is formed of Al phosphate, green soap, rosin oil, a sulfonated oil such as Turkey red oil and coloring matter, e. g., C black and Milori blue.

Writing ink. J. W. BALSER. U. S. 1,439,658, Dec. 19. PhOH 34 oz., denatured alc. 60 oz., H_2O 20 oz., sugar 13 oz. and "Diamond Dye" or other dye 1 oz.

Copying ink. M. SHINOZAKI. U. S. 1,439,489, Dec. 19. Copying ink is formed of a dil. aq. soln. of HCl, a soln. of methyl violet in H_2O and a filtered aq. soln. of fufuril.

"Antismearing composition" for printing inks. L. L. PARKAS. U. S. 1,439,623, Dec. 19. Ppdt. $CaCO_3$ 7, ZnO 3.5, $BaSO_4$ 1.75 and rapeseed oil 8 parts, by vol.

Collecting fumes from fatty substances. P. W. WEBSTER. U. S. 1,438,565, Dec. 12. Fumes such as are evolved in heating fatty animal or vegetable substances, e. g., in the manuf. of varnishes, are subjected to surface condensation to sep. a portion of the fume and are then scrubbed successively with H_2O and with an alk. soln. such as $Ca(OH)_2$ or NaOH. Cf. C. A. 16, 4358.

Wood filler. O. V. STEWART and A. R. HATZFELD. U. S. 1,438,618, Dec. 12. Shellac 50 oz., alc. 1 qt. and whiting 106.5 oz.

Furniture polish. R. A. KLOHN. U. S. 1,438,118, Dec. 5. Paraffin oil 2 qts., alc. 36 oz., gum mastic 1 oz., H_2O 14 oz., vinegar 4 oz., turpentine 4 oz., butter of antimony 3 oz. and oil of citronella 2 oz.

Flexible coating for fabrics. H. BRUYN. U. S. 1,437,397, Dec. 5. A flexible coating for preserving exposed fabrics such as wagon tops or tarpaulins is formed from boiled linseed oil 4, pulverized charcoal 2 and an aq. satd. soln. of "green fig soap" 3 parts.

Linoleum. A. B. CRAVEN. U. S. 1,438,221, Dec. 12. An agglutinant for linoleum is prepd. by subjecting a mixt. of oils (having some drying properties) and their fatty acids, *e. g.*, a mixt. of products of linseed, soy-bean or whale oil, to distn. out of contact with free O , to distil off non-drying material and obtain a residue which goes beyond the varnish stage and becomes semi-solid, resilient, tacky and adhesive. U. S. 1,438,222 relates to a similar process in which the residue of the distn. is oxidized by air at 80–110°. Co resinatc may be added.

27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

Bibliography on the production of fatty substances. D. MONTEL. *Bull. mat. grasses inst. colonial Marseille* 1922, Nos. 9 and 10, 237–300.
E. J. C.

Hardened fats. P. SHESTAKOO AND P. KUPCHINSKII. *Z. deut. Oel-Fett-Ind.* **42**, 741–6, 757–9, 774–6(1922).—The work was undertaken to establish methods for the technical valuation and the detn. of the chem. constitution of hardened oils. A detailed account with numerous tables and curves is given of exptl. results of hardening cottonseed, sunflowerseed, hempseed and linseed oil, and the conclusions are as follows: (1) Hydrogenation of oils takes place by partially satg. the more unsatd. acids. At the same time but at a much slower rate the less unsatd. acids become fully satd. In sunflower-, hemp- and linseed oil all unsatd. acids have become oleic acid at 54 I no.; in cottonseed oil at 34.2 I no. (2) For each type of oil there exists a fixed relationship between titer and I no. and the compn. of the oil at any stage during hydrogenation can be calcd. and the curves can be used to identify the nature of the oil and the degree of hydrogenation. (3) The titer of a mixt. of satd. and unsatd. acids does not depend upon the structure or the no. of double C atoms of the unsatd. acids but only upon their quantity. (4) With equal titers the hardened fats have a much higher I no. than the natural fats; it is possible to distinguish a natural fat from a hardened oil or from a mixt. of hardened with non-hardened oil. (5) A mixt. of hardened oil with non-hardened oil has a higher I no. of the acids than either the acids of a natural fat or of a single hardened oil. A hardened oil to be of equal technical value as a natural fat must possess acids of 35–40 I no., never above 45.
P. ESCHER

Variation in Lovibond color readings of coconut oils. P. W. TOMPKINS. *Cotton Oil Press* **6**, No. 7, 30–1(1922).—Results on the color of 2 coconut oils by 5 labs. clearly indicate a need for greater uniformity of procedure. In both the light and the dark sample the difference in yellow was 80. The variation in red for the light oil was 3.2 and for the dark 6.4. Some of this disagreement is due to the reading of color in different kinds of light and some to lack of any agreement in the ratio of yellow to red glasses. It is suggested that a ratio of 1 red to 6 yellow be maintained as far as possible.

H. S. B.

The manufacture, testing and uses of wool fat. G. HARTMANN. *Chem. Weekblad* **19**, 117–9, 143–6(1922).—Largely a repetition of previous articles (*C. A.* **15**, 443, 769,

1411) with the addition of a brief history of wool fat and lanolin, their uses and methods of testing. In the charcoal used for bleaching the lanolin soln. (C. A. 15, 1411) there remains an aliphatic alcohol only slightly sol. in C_6H_6 , which may be dissolved out with hot $EtOH$. This will absorb a greater quantity of H_2O than anhyd. lanolin. Three parts of a mixt. of 2% of this alcohol and 98% of ceresin and vaseline when beaten up with 1 pt. of H_2O make a good snow-white salve base. The recovery of wool fat from scouring water involves considerable loss of fat and K salts. H. has patented a process for leaching the wool with a solvent which later is expelled by water. This removed the K salts. He claims a recovery of 20% of the wt. of wool as fat and 4.3% as K_2O . $KMnO_4$ soln. made acid with H_2SO_4 is a good bleaching agent for crude wool fat. To bleach with $KClO_3$, 200 kg. of raw fat and 200 l. water are treated with an aq. soln. of 2 kg. $KClO_3$ and 1200 g. oxalic acid at 105° until there is strong odor of Cl . Then 500 g. of oxalic acid in 200 l. of water are added and the batch is again boiled and finally this treatment again repeated. After settling and drawing off the soln. the fat is washed with water until free from acid. Wool fat makes a good base for heavy lubricants, especially when treated with lime water. Such greases are used in rolling mills; they often contain rosin and rosin oil. Mixed with neatsfoot oil, tallow, paraffin, or ceresin and lamp black wool fat is found in many belt and harness dressings. It is also used in filling heavy cables and ropes, especially where these are employed in rope drives. The pure lanolin is employed as a salve base and in medicated soaps. It should not darken when heated to 140° and in bright sunlight will bleach at this temp. One g. of pure lanolin heated with 10 g. glacial $AcOH$ gives when cooled and treated with 10 drops of concd. H_2SO_4 a brownish yellow. The impure material turns dark green in 30 min. Cl is detected by heating an alc. soln. of lanolin with a little dil. HNO_3 , filtering and testing the filtrate with alc. $AgNO_3$.

H. S. BAILEY

Ishinagi- and Abura-Bodzu liver oils. MITSUMARU TSUJIMOTO. *Chem. Umschau Fette, Oele, Wachse u. Harze* 29, 385-7 (1922).—Both oils have a strong odor. The const. of Ishinagi liver oil (3 samples) and of Abura-Bodzu liver oil (1 sample), resp. are: d_4^{20} 0.9359, 0.9338, 0.9280, 0.9188; acid no. 0.62, 3.2, 4.27, 7.9; sapon. no. 108.3, 127.1, 152.3, 176.3; I no. (Wijs) 198.5, 177.8, 170.7, 111.2; n_D^{20} 1.5498, 1.5297, 1.5030, 1.4761; unsapon. 50.64, 38.08, 20.32, 4.17%; glycerol —, 3.20, —, —. In case of the former oil the fatty acids have m. p. $42-43^\circ$, neutn. no. 196.2, I no. (Wijs) 86.3, and polybromides 1.4%; the unsapon. matter has cholesterol 44.97%, I no. 201.8 and I no. of stearin-free unsapon. matter 248.2. Hydrocarbons are absent from the unsapon. matter of Ishinagi-oil. Both oils give a violet color reaction with concd. H_2SO_4 , which is strongest in their unsapon. matter. In acetic anhydride soln. this color is blue instead of violet.

P. FISCHER

Lamella experiments on colloids. LEGRADI. *Seifensieder Ztg.* 49, 730-2 (1922).—Leimdörfer (cf. C. A. 16, 4081) has compared the salting out of curd soap and its subsequent boiling to form a "closed" soap with the analogous swelling of rubber in some solvent. This idea is further developed by Legradi by expts. on the swelling capacity of soaps of known compn., by cutting two 3 mm. thick strips of soap, $7\frac{1}{2}$ mm. wide and 30 mm. long, uniting them at one end by another strip of soap 10×20 mm., leaving a space of 5 mm. between the two legs and hanging one leg of this horseshoe (total wt. 2.1 g.) over the edge of a test-tube filled with CO_2 -free H_2O , allowing the other leg to hang outside of the tube and placing a series of such tubes in a glass case contg. a dish with H_2O in order to retard evapn. By comparing the appearance of the soap-strips at intervals, a rough measure of the swelling capacity of the soaps is obtained. 1. operated on the following mixts. (1) A soap base of 80% tallow and 20% coconut oil. (2) The same made into a 63% curd soap. (3) The same with 10% rosin and contg.

64.5% fatty acids. (4) The same made into a soap of 250% yield and slowly dried to a 60% fatty acid content. These 4 samples were Na soaps. (5) A K stearate soap of 65% fatty acids. (6) The same made into a 100% yield and slowly dried to a 67.5% content. (7) Com. K soap of 211 sapon. no. and 68% fatty acids. Temp. 23–30°. The results show that (1) gave the least and (7) the greatest loss in wt. These results were confirmed by using 50-g. prisms of the same soaps for hand-washing expts. L. finds that a 100-g. cake will furnish about 500 hand washings. P. BSCHNE

Reactions in the soap kettle from a colloid-chemical standpoint. II. The role of viscosity. J. LEIMDÖRFER. *Seifensieder Ztg.* 49, 746–7, 762–3, 774, 789, 799–800 (1922); cf. C. A. 16, 4081.—No fixed rules or tables can be formulated for the proper boiling of soaps because the compn. of the fats used varies. (1) Cold-made soaps. All the ingredients are agitated in the kettle until the thin liquid emulsion forms a thick viscous mass; then agitation is stopped and the reaction allowed to go automatically to completion. If the agitation is stopped before the fixed degree of viscosity is reached, a lye-spotted, partly unsaponified mixt. results; if carried too far, a stiff mass is the product. (2) Semi-boiled soaps. If the ratio of lye to fat is improperly chosen, the product, especially with filled soaps, will be too viscous and show insufficient hardness, dark color and unusual transparency, or it will not be viscous enough and lye will sep. or will yield a spotted soap. (3) Bschweiger soaps. This type is a half-curd soap whose sapon. is limited on the one side by curdling of the partly saponified fat and on the other side by the formation of a smooth non-mottled "closed" soap. If the amt. of coconut oil has been small, then 0.1% of the salting-out medium may have a deciding influence. (4) Curd soaps. The proper viscosity is reached when the curd seps. as a homogeneous mass over the lye without occluding any of the latter. (5) Soft soaps. Unshortened soaps have insufficient consistency, glide too much and become rubbery and sometimes turbid when too much H₂O is present. When over-shortened, they sep. lye and lump together. Neither type forms granules. Colloidal viscosity is not an expression of the inner friction between the suspended particles, but the particles are capable of coupling together into a system, thereby curtailing their previous individual freedom of motion to make it subservient to the requirements of the group-motion as a whole. Curdling ("Zusammenfahren") of half-saponified soap. If the weak soap in the kettle loses its excess of alkali in the presence of large amts. of fat, the latter may become absorbed by the former, the soap losing its swelling capacity and expelling H₂O; this is accompanied by an explosive noise and the formation of tulip-flowers as the steam breaks the surface of the thickened mass. It is prevented by allowing only a limited fat absorption by the much diluted soap, or by adding NaCl which decreases the viscosity and prevents the formation of fat-soap conglomerates with their tough texture and slow soln. This addn. of NaCl to decrease viscosity is especially desirable in saponifying fatty acids by means of Na₂CO₃, thereby allowing a free escape of the liberated CO₂ gas, and also in converting the lime soap in the Kriebitz process into Na soap. The reverse of this phenomenon is observed when soaps are decomposed by strong acid, forming soap-fatty acid conglomerates which are broken up only by long continued boiling. Cold-made soaps yield the smoothest, non-brittle product when some fat remains absorbed by the soap; some unsapon. oil is usually added to allow this oil-absorption. Such additional unsapon. oil also decreases the great swelling capacity of this type of soaps and their too rapid soln. when being used. Soap fillers. The filling of soaps means the change in viscosity from a properly "closed" soap to that of a curd soap but not sufficiently far to salt it out. The addn. of electrolyte solns. is limited on one side to obtain the proper "yield" of soap and on the other to obtain correct hardness. If the concn. of the electrolyte soln. is too great, the homogeneity and smoothness of the product will be disturbed; if too low, the viscosity will increase, but the cellular

structure of the soap will not possess sufficient hardness for a good cake of soap. In such a case the addn., even of small amts. of some protective colloid will remedy the over-shortening. Eschweger soaps have a characteristic mottled appearance; there are two soln. systems side by side that do not sep. from each other during cooling. If the required viscosity is not reached the marbling will be insufficient. Over-salting of curd soaps can be remedied by further boiling with direct steam or by the gradual addn. of small portions of weak brine. By detg. the sp. gr. of the lye of a properly boiled charge, and comparing it with the sp. gr. of the next charge the over-salting of the next charge can be prevented, if the fats are of like character. A good soft soap furnishes a yield of 230-250% of 40% fat content; this is obtained by allowing a certain excess of alkali or by adding carbonate or KCl or both. If stearin is present in the fat mixt. it will sep. out on cooling as a stearate salt and deposit the characteristic granules all through the mass. Characteristic behaviors of the various soaps on dropping from a spatula or a shovel are described.

P. ESCHER

Inflammatory effects of some toilet soaps. E. LUBLINSKI. *Seifensieder Ztg.* 50, 4-5(1923).—Cases are cited in which coumarin has caused skin irritation. P. E.

The use of bleaching agents in laundries. W. KIND. *Seifensieder Ztg.* 49, 761-2, 773-4, 785-6, 798(1922).—An extended discussion of the value of O-carrying agents ("Persil") compared with Cl bleaching in laundry practice. Four series of wash expts. giving the action of cleansing and bleaching agents upon the strength of fabrics are described. After washing the test strips 40 times under stated conditions the fiber strength was detd. on the Schopper app. at 20 cm. test length with the following results, expressed in % of original fiber strength: (1) soap powder 88%, (2) soap powder with subsequent chlorination 68.6%, (3) "Persil" 73.3%, (4) Cl-water 86.7%. It is pointed out that chlorination necessitates the subsequent use of some anti-chlor agent, because Cl forms compds. with the protein of linen fibers which persistently retain an objectionable Cl odor.

P. ESCHER

Yield of soap. J. DAVIDSON. *Seifensieder Ztg.* 48, 813-4(1922).—A discussion of the customary calcn. of the yield of soap by the formula: % fatty acids in the finished soap: 100 = % fatty acids in the oil: yield. Any discrepancy between calcn. and practice is ascribed to the volatility of lower fatty acids when drying at 100° during analysis or to the presence in the fats of hydroxy acids or unsaponifiable substances.

P. ESCHER

Modern edible-oil manufacture by extraction followed by refining. A. VON HEYMANN. *Seifensieder Ztg.* 49, 814(1922).—It is stated that the new rotating vacuum extn. plants are cheaper than expression app. and produce a residue contg. 1% oil, and even this small amt. may be reduced to 0.1% with modern appliances. P. E.

The unsaponifiable constituents (higher alcohols) of shark and ray liver oil. YOSHIIYUKI TOYAMA. *Chem. Umschau* 29, 237-40, 245-7(1922).—I. *Rabukazame oil*.—T. examd. 4 samples of liver oil of the Rabukazame shark (*Chlamydoselachus anguineus* Garman). Nos. 1, 3 and 4a were from females, No. 2 from a male, while No. 4b was obtained from the liver of one of the 6 embryos found in 4a.

Rabukazame oil.

	No 1.	No. 2.	No. 3.	No. 4a.	No. 4b.
D ₁₅ ^o	0.885	0.8747	0.8749	0.8756	0.8818
Acid no.	0.47	0.66	0.60	0.23	0.57
Sapon. no.	115.8	94.0	93.4	97.8	116.5
I no. (Wijs)	130.3	136.3	134.4	112.1	112.3
n _D ₂₀	1.4725	1.4724	1.4716	1.4703	1.4704

% unsapon.	37.06	51.53	51.65	49.64	39.12
Acid no. of fatty acids	—	183.9	—	182.8	189.8
I no. fatty acids	—	84.8	—	77.6	99.7
Bromide no. of fatty acids	5.58	—	4.80	—	—

All of the samples contd. squalene, forming squalene hexahydrochloride when HCl gas was passed through the ether soln. of the oil. Elaborate examns. were made of the unsapon. matter of these oils, the methods employed being outlined at the various steps and sepn.

Unsapon. matter of Rabukazame oil.

	No. 1.	No. 2.	No. 3.	No. 4a.	No. 4b.
n_{20}	1.4770	1.4742	1.4741	1.4699	1.4681
I no.	185.7	179.9	190.8	188.2	129.5
Sapon. no. of acetyl ester	135.7	135.1	132.4	158.5	166.6
% cholesterol	—	2.60	—	—	—

II. The unsapon. matter of various shark liver oils.—The original oils from which the unsapon. matter was sepd. had the following constns.:

	Kanatsubo- zame.	Kuroko- zame.	Kurozame.	Itachi- zame.	Abura- zame.	Aizame.
D_{15}^0	0.8890	0.8917	0.8816	0.9108	0.9162	0.8767
Acid no.	0.20	5.10	0.88	0.26	0.36	0.22
Sapon. no.	98.1	92.1	70.9	174.0	174.9	54.0
I no.	191.5	213.7	225.0	75.2	118.5	259.8
n_{20}	1.4791	1.4812	1.4825	1.4680	1.4734	1.4860
% unsapon.	48.51	53.06	57.17	11.48	12.68	71.38
Zoölogical name						

*Szymnor-
hinus licha-
tium Ritteri*
(Bonna-
terre) Jordan &
Fowler

*Galeocerdo
tigrinus*
Müller &
Henle

*Ileptan-
chias deani*
Jordan &
Starks

*Centro-
phorus.*

In the case of the unsapon. matter of the last two in the above table the I nos. were, resp., 66.2 and 76.0, and the sapon. nos. of the acetyl product were, resp., 261.8 and 248.3. III. Summary.—(1) The principal constituent of the unsapon. matter of Rabukazame oil is octadecenol; the oil contains considerable squalene and some cetyl alc. and cholesterol. (2) The unsapon. of Auburazame and Itachizame oil consists almost exclusively of selachyl and batyl alc. (3) The unsapon. of Kanatsubozame and Kurokozame oils contain selachyl and batyl alcs. and in addn. also much squalene. (4) The unsapon. of the com. Aizame and Kurozame oil contain also selachyl and batyl alcs. and much squalene.

P. ESCHER

Remarks on the decolorization of vegetable oils. M. J. VAN TUSSENBROEK. *Chem. Weekblad* 19, 266-7(1922).—Vegetable oil is decolorized by shaking with adsorption C. The degree of decolorization is found to depend also on the acidity of the oil. To test this, very pure coconut oil is colored first with 1% aminoazobenzene. 100 cc. of this oil is then mixed with various quantities of pure AcOH, ranging from 0.2 to 2.0 cc., and shaken with 1% "Norit" for 1 hour at 90°. The decolorization is best in the samples contg. 1.4 to 1.6 cc. AcOH per 100 cc. oil.

R. BRUNNER

Determination of the fat content of foods and soap (GROSSFELD) 12. Cotton

softeners (ESTEV) 25. Scheme for estimating the washing and cleansing actions of detergents (HEERMANN) 25.

GILL, AUGUSTUS H.: *Short Handbook of Oil Analysis*. 10th Ed. revised. Philadelphia: J. B. Lippincott Co. 223 pp.

Extracting grease from garbage or other solid materials. F. J. STOKES. U. S. 1,438,194, Dec. 12. Garbage, fish scrap, slaughterhouse refuse, etc., are freed from air and vapor by subjection to a vacuum while cold and before breaking the vacuum the material is treated with a solvent of grease or fat.

Apparatus for extraction of oils or fat. J. ARH. U. S. 1,437,743, Dec. 5. A jacketed extn. chamber for extn. of oils or fats from solid materials is provided with horizontal heating pipes extending through its upper portion to effect uniform heating. The solvent used is repeatedly distd. and returned to the extn. chamber.

Sulfonic acids for splitting fats. R. E. DIVINE. U. S. 1,438,101, Dec. 5. A soln. of $\text{Al}_2(\text{SO}_4)_3$ is mixed with petroleum sulfonic acid sludge, the mixt. is boiled, the ppt. which forms is sepd. and washed repeatedly with H_2O until the wash liquor is no longer discolored and the ppt. is then hydrolyzed with H_2SO_4 and the liberated sulfonic acids are sepd. from associated H_2SO_4 and sulfate by stratification.

Catalyzer for oil hardening. C. ELLIS. Can. 226,305, Nov. 21, 1922. A catalyzer suitable for the hydrogenation of fatty oils is made by incorporating a basic compd. of a metal of the Ni group with a waxy vehicle, heating the mixt. above 300° whereby cracking of the wax and reduction of the metal compd. occur and agitating the mixt. during the process.

Lathering soap. A. VOGES. U. S. 1,438,199, Dec. 12. Small quantities of liquid soap are discharged into air jets, to produce a lather.

Cleansing compositions. G. W. SMITH. Brit. 180,957, Sept. 29, 1921. A prepn. for cleaning clothes, etc. consists of a mixt., preferably in the proportions stated, of castile soap 8 oz., soda 4 oz., salt 1 oz., lime 1 oz., sodium metaborate 1 oz., naphthalene 1 oz., and gas liquor 8 drams. For use one part of the prepn. is mixed with 2 parts of hot H_2O .

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

History of diffusion in Mauritius. P. DE SORNAY. *Rev. agr. Maurice* 1, 132-5 (1922).

F. W. ZERBAN

History of juice sulfitation. P. DE SORNAY. *Rev. agr. Maurice* 1, 130-2 (1922).

F. W. ZERBAN

Clarification practice. W. R. MCALLEP. *Facts about Sugar* 16, 30-1 (1923).—This is an account of the recent modifications introduced in Hawaiian sugar mills. Sixteen out of 22 factories are employing a more alk. clarification. From data cited it appears that the continuous addition of lime at the mill has not been particularly successful in practice. The general opinion with regard to returning settlings to the mill is that it will cause a decrease in extn.

N. KOPELOFF

The lime-carbon dioxide purification (of beet juice). DUTILLOV. *Bull. assoc. chim. suc. dist.* 40, 75-82 (1922).—In the carbonatation of beet juice it is essential that the first carbonatation be stopped at an alky. of 0.8-0.9 g. CaO per 100 cc. If the alky. is

greater, filtration is difficult; if less, the impurities and coloring matter sepd. in the foam redissolve in the juice. Rapid carbonatation is desirable because of these advantages: (1) an increase in purity of the juice, (2) a better color, (3) an easier filtration. The temp. of the carbonatation, the purity of the CO_2 , and the quality of the limestone are not primary factors.

W. L. McCABE

Return of runoffs. P. FAYD'HERBE. *Rev. agr. Maurice* 1, 116-21 (1922).—The present methods of making as much white sugar as possible and final molasses require too much fuel, labor and pan capacity, frequently yield sugar of inferior grade and keeping quality, and necessitate the use of such large quantities of SO_2 that there is distinct danger of inversion. All these objections are overcome by the following process which has been used successfully in practice. A first massecuite (preferably from sirup only) is run into crystallizers which are divided into 2 series, A and B. The runoffs from a previous strike of first massecuite which runoffs have been sepd. into high and low, either by the usual method or by double purging, are, without any previous treatment whatever, drawn into a vacuum app. and boiled separately to supersatn. To prevent crystn., the runoffs thus coned. are slightly overheated before being dropped. The coned. high runoffs are then added to massecuite A, and the low ones to massecuite B. After the massecuites have cooled completely in the crystallizers, they are purged separately, the runoffs of either again being divided into high and low. The high runoffs from massecuites A and B can be mixed and used again for massecuite A. The low runoffs which are used in massecuite B will yield final molasses. This mode of working saves steam, because only high-purity massecuites are boiled directly to grain, and because the runoffs are not dild. before being coned. again. The blowing-up of runoffs is avoided, thus saving labor and power. No additional clarification of runoffs is required. The sugar produced is of good quality and keeps well; its color is better, because the runoffs are not boiled in the pan where the crystals would be liable to partial caramelization. Figures are presented to prove the assertions made. F. W. Z.

Massecuites. P. DE SORNAY. *Rev. agr. Maurice* 1, 135-7 (1922).—Av. wts. of massecuites of different grades to be obtained from a ton of cane of varying sugar content or from a certain wt. of first massecuite are given, and it is shown how these data can be used to calc. the amt. of sugar in process, for purposes of chem. control. F. W. Z.

Further analyses of Ceylon-grown canes. M. K. BAMBER. *Tropical Agriculturist* 58, 205-7 (1922).—Chem. analyses are given of the juice from 21 varieties of cane.

M. S. ANDERSON

Scale. P. DE SORNAY. *Rev. agr. Maurice* 1, 137-8 (1922).—The analyses of 3 boiler scales from different localities in Mauritius are given and correlated with the compn. of the boiler feed water. The scale in effects consists principally of org. matter, CaSO_4 , SiO_2 , salts of Mg, and also Ca phosphate where P_2O_5 is used in clarification. In the first two bodies of a quadruple effect the org. matter is higher than in the last two, while the CaSO_4 increases from the first to the fourth. The scale in the last body is also high in SiO_2 , and its removal is therefore more difficult. F. W. ZERBAN

Gelose and the algae which produce it. C. SAUVAGEAU. *Bull. sci. pharmacol.* 29, 637-41 (1922).—A review. F. S. HAMMETT

The inversion of sucrose by alkaline cupric solution. L. MAQUENNE. *Bull. soc. chim.* 31, 799-806 (1922).—A criticism of the report of Canals (*C. A.* 17, 371) and a resumé of work of M. previously reported; cf. *C. A.* 10, 980, 1108, 1280. I. P. ROLF

Apparatus for mixing lime and sugar juice or other liquids (U. S. pat. 1,438,843) 1.

Extracting sugar from shredded beets. W. C. GRAHAM. U. S. 1,437,801, Dec. 5,

Extg. liquid under pressure is forced upwardly through a mass of shredded beets compacted together and moving downwardly through an extn. vessel with a constricted discharge opening for the solid residue at its bottom.

Centrifugal sugar-washing apparatus. W. W. HARTMAN. U. S. 1,439,676, Dec. 19.

Filtering apparatus for sugar solutions. R. VACHIER. U. S. 1,438,797, Dec. 12. Filter frames are mounted on a hollow revoluble shaft in a tank with perforated spray pipes between them.

Decolorizing carbon. C. S. HUDSON. U. S. 1,438,113, Dec. 5. Sawdust, corn cobs, scrap leather or other carbonaceous material is impregnated with H_3PO_4 , H_2BO_3 , or other fusible acid and the impregnated material is heated to about 400–600° to effect carbonization and obtain a product suitable for treating sugar solns.

29—LEATHER AND GLUE

ALLEN ROGERS

The manufacture of chrome ooze calf. W. C. JACKSON. *Am. Dyestuff Rep.* 11, 297–8(1922).—The best leather is made from $\frac{1}{8}$ lb. green salted skins and skins much heavier or lighter should not be used. Tanning is most suitably carried out in a glucose one-bath liquor. After tanning, the skins should be neutralized, split to 3 oz., fat-liquored with egg yolk and flour, then dried and staked. They should be buffed on a 22-in. overshot, crown face wheel, speed 1650 r. p. m., first with no. 100 then with no. 200 emery. Directions are given for dyeing the skins black, brown or gray. I. D. C.

The neutralization of chrome leather. LOUIS MEUNIER AND PAUL CHAMBARD. *Cuir* 12, 4–7(1923).—In chrome tanning the hide fixes (a) free H_2SO_4 liberated by the hydrolysis of the basic Cr salt, (b) a complex of H_2SO_4 and Cr_2O_3 . Neutralization with soap solns. removes part of the total SO_4 , while the free fatty acids are adsorbed and not changed to a chrome soap. Part of them are oxidized to acids insol. in petr. ether or benzene. Neutralization and fat-liquoring may therefore be combined in one operation provided sufficient soap is present in the fat liquor to stabilize it and to neutralize the SO_3 . With Na silicate, the NaOH liberated by hydrolysis neutralizes the leather while the colloidal silicic acid is adsorbed by the hide fibers, yielding a white leather, liable to crack if excess silica be present but non-slippery on wet ground. $NaHCO_3$ and borax completely neutralize SO_3 both free and in the complex. Used in excess, the grain dries to a horny surface. With $Na_2S_2O_3$, all free S liberated is fixed by the leather and this reagent may be used in excess with no danger. With Na_2HPO_4 , the acidity is unchanged, but all SO_3 is replaced by PO_4 , and the leather takes on a characteristic green color. Total SO_3 in a chrome leather may be estd. by extg. the macerated leather with a known amt. of 0.2 N $NaHCO_3$, filtering, and titrating an aliquot of the filtrate. All expts. were made on leather tanned with a basic chrome alum soln.

F. L. SEYMOUR-JONES

The influence of moisture on the extraction of oils and greases from leather. A. M. HAY. *J. Soc. Leather Trades' Chem.* 6, 385–9(1922).—Extns. with petroleum ether and $CHCl_3$ were made of portions of leather, (1) in the air-dry condition, (2) after drying at 105°, and (3) after exposure for 24 hrs. to an atm. satd. with moisture. The amt. of ext. increased as the moisture content of the leather increased. This was probably due to the extn. of some H_2O -sol. material by the H_2O which was present in the leather or solvent. Almost as much material was extd. from leather which had been dried and remoistened as from the undried leather. This effect of moisture is more pronounced with $CHCl_3$ than with petroleum ether. I. D. C.

Notes on the extraction of oils and greases from leather. G. W. SCHULTZ. *J. Soc. Leather Trades' Chem.* 6, 389-93(1922).—A discussion of the relative efficiency of petroleum ether and CHCl_3 . In previous work it was shown (cf. *C. A.* 15, 4058) that in the case of a leather extd. first with petroleum ether and then with CHCl_3 , only $\frac{1}{4}$ of the CHCl_3 ext. was fat. The % error in the results for total fat was, with CHCl_3 , +25% and with petroleum ether -7.2%. The high results with CHCl_3 were found to be due to the extn. of tannins etc. by the moisture of the leather. This finding has been confirmed by later work (cf. *C. A.* 16, 2618). S. makes the following criticisms of the work of Veitch and Hunt on the extn. of oils and greases from sand (cf. *C. A.* 13, 3037); the conditions under which the extd. oil and grease was dried were such that there was a loss of oil in some cases and also the presence of impurities (soaps, tarry matter, moisture etc.) in the oils was not taken into consideration. It has frequently been pointed out that drying oils are not sol. in petroleum ether after oxidation and polymerization; still an oil contg. oxidized fatty acids may be entirely sol. in petroleum ether. For the extn. of oils and greases from leather S. suggests a double extn., first with petroleum ether and then with another solvent to remove oxidized oil or grease. I. D. C.

Waterproof tests on commercial and experimental leathers. D. WOODROFFE AND W. R. MORGAN. *J. Soc. Leather Trades' Chem.* 6, 393-9(1922).—Of the leathers tested only stuffed vegetable-tanned leather possessed any considerable degree of waterproofness. Fat-liquored vegetable-tanned leather was rather easily penetrated. Chrome leather, which is very open, is not made waterproof by the ordinary fat liquors or stuffing greases. I. D. C.

Rules for sampling and analysis of quebracho extract. VENTURA MORERA. *Anales assoc. quim. Argentina* 10, 189-98(1922).—Proposed rules. L. E. GILSON

Lime-water method for the acidity of tan liquors. F. L. SEYMOUR-JONES. *J. Soc. Leather Trades' Chem.* 6, 399-401(1922).—Proctor's lime-water method cannot be used for detg. the approx. acidity of gambier solns. since gambier is not pptd. by $\text{Ca}(\text{OH})_2$; it is however pptd. by $\text{Ba}(\text{OH})_2$. But titration of a no. of tan liquors with both $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ showed that the ratio of the amts. of each required was not const. and that $\text{Ba}(\text{OH})_2$ offered no advantages. I. D. C.

Pit tannage with oak bark and the role of enzymes. E. SCHELL AND U. J. THUAU. *Cuir* 12, 2-3(1923).—Tannins exist in oak bark partially esterified with acids and partially as anhydrides in the form of glucosides. This complex mol. is far less reactive than the mol. of the tanning principle when split off. Some enzymes, e. g., tannase, possess the power of splitting up the complex mols. and releasing the more active tanning principle without further hydrolyzing it to non-tans. This causes a change from a simple adsorption of tanning matter to a chem. combination between tannin and hide. The heat employed in the manuf. of tanning exts. destroys all enzymes and hence renders the exts. less reactive. In time enzyme preps. will be added to exts. after manuf. to activate them. Nothing is known of the optimum conditions of temp., etc., for the action of these enzymes on tannins. F. L. SEYMOUR-JONES

The tannin of the native (German) oaks (FREUDENBERG, VOLLBRECHT) 10. Treatment of tannery wastes to prevent stream pollution (BESSELIEVRE) 14. Colloid chemistry of basic chromic solutions (SEYMOUR-JONES) 2. Metallopyrophosphoric acids or their salts [for tanning] (CAN. pat. 226,670) 18.

Tanning substances from phenols and formaldehyde. R. B. CROAD AND G. E. KNOWLES. U. S. 1,437,726, Dec. 5. CH_2O or its polymerization products are condensed

with at least 2 mol. proportions of mixed cresols or similar aromatic hydroxy compds. by heating with NaHCO_3 or other alk. condensing agent, then cooling somewhat, sulfonating with 1-2 mol. proportions of H_2SO_4 and partially neutralizing with NaOH so that 1 g. of the finished product requires 1.0-1.4 cc. N NaOH for neutralization. Cf. *C. A.* 17, 226.

Extracting gelatin. C. COLLARD. *Brit.* 166,896, July 23, 1921. A series of digesters is charged with ossein and heated by external circulatory heaters. The ext. from the first digester is heated until the gelatino-meter shows 2% and is then passed in stages through the other digesters each time meeting ossein which has had one fewer treatment. In the last digester it meets fresh ossein.

30—RUBBER AND ALLIED SUBSTANCES

JOHN D. TUTTLE

Colloid chemistry and rubber. R. WEIL. *Kolloid-Z.* 31, 303-8(1922).—A general survey in its colloidal aspects of the rubber industry from the latex to reclaiming.

C. C. DAVIS

Rubber. RUDOLF PUMMERER AND PETER A. BURKARD. *Ber.* 55, 3458-72(1922).—A study of the structure of the rubber mol. by means of its hydrogenation and oxidation. **Hydrogenation.**—Though previous attempts at hydrogenation had failed (cf. *Ann.* 406,200(1914); Harries, *C. A.* 16, 1953; Harries, *Kautschuk*, p. 48), this was accomplished by first depolymerizing the rubber as much as possible and then effecting hydrogenation with H in the presence of Pt black as catalyst. By this method rubber combined with 1 mol. of H for each double bond and for each isoprene group according to the equation: $(\text{C}_5\text{H}_8)_x + x\text{H}_2 \longrightarrow (\text{C}_5\text{H}_{10})_x$. The reaction took place in cold petroleum-hexane but was more easily carried out at 70-80° with a 0.5% hexahydrotoluene soln. of rubber freshly purified by the method of Harries and with the freshest possible Pt black. With rubber solus. over 1%, hydrogenation was incomplete, perhaps because of adsorption of rubber by the Pt. Exptl. results of the absorption of H coincided closely with the equation above. There was no tendency to absorb more H than that corresponding to the formula $(\text{C}_5\text{H}_{10})_x$. If rubber contd. an open chain 1 more mol. of H would be absorbed thus: $(\text{C}_5\text{H}_8)_x + (x+1)\text{H}_2 \longrightarrow \text{C}_{5x}\text{H}_{10x+2}$. The actual H absorption indicated for rubber either a ring structure or an extremely long chain of isoprene mols. with $x > 20$. By filtering off the Pt and by evapg. the hexahydrotoluene, a pale yellowish hydrocarbon was obtained conforming to rubber in its empirical formula $(\text{C}_5\text{H}_8)_x$. This was designated *iso-rubber II*. Unlike rubber, it dissolved rapidly in Et_2O , but was insol. in Me_2CO . After long standing it dissolved in Et_2O only after previous swelling. The yield was almost quant. If rubber consisted of isoprene mols. bound by secondary valences, no rubber would have remained on hydrogenation and after evapn. **Isolation of hydro-rubber.**—Only by pptg. the Pt with kaolin in the absence of air, centrifuging and evapg. to dryness *in vacuo* at 0° could the hydro-rubber be obtained. Both in soln. and in the dry state, it was unstable in the air. Repeated soln. and centrifuging failed to remove traces of Pt. The film of hydro-rubber remaining after evapn. and drying *in vacuo* was similar to rubber in elastic properties but was pale yellowish. It swelled in Et_2O and dissolved after several hrs. No mol. wt. detn. was made but analysis showed it to correspond to $(\text{C}_5\text{H}_{10})_x$ based on a mean value of 11.85% for the original rubber. The unstable combination of H in this hydro-rubber indicated that perhaps the H was not united by its primary valences to the rubber nucleus. Against the presence of a secondary combination of the colloid with mol. H was the stability in a vacuum

of 1 mm. It is suggested that strains exist in the rubber ring and that these increase upon satn. with H, causing the instability of the hydro-rubber. *Autoxidation of hydro-rubber*.—The hydrogenated reaction mixt. freed of H by evacuation, but without removal of Pt, was shaken with O. Absorption was at first rapid then decreased to a rate comparable to that of a similar concn. of rubber in hexahydrotoluene. The autoxidation product, which was iso-rubber H, dissolved rapidly when fresh in Et₂O by rubbing. *Hydrogenation of iso-rubber H*.—Treated with H and Pt black, it rapidly absorbed 1 mol. of H per isoprene nucleus. It therefore contd. no bridging groups. No further investigation was made. In soly. it resembled the α - and β -iso-rubber of Harries rather than ordinary rubber, and might possibly be the depolymerized Et₂O-sol. form mentioned by him. *Oxidation of rubber by gaseous O*.—Absorption of O by a very dil. hexahydrotoluene soln. of rubber at 22° ceased when 0.5 mol. of O per 1 isoprene nucleus was absorbed. This condition was reached regardless of whether Pt black was present. With more concd. solns. the reaction was extremely slow. *Oxidation by perbenzoic acid*.—By treating a CHCl₃ soln. of rubber with perbenzoic acid at 0°, concg. *in vacuo* at room temp. and adding pentane, a pure white tough ppt. of rubber oxide was obtained corresponding to (C₈H₈O)₂. It was much less elastic than rubber and when dry was insol. in the usual rubber solvents. The yield was 3.51 g. per 2.89 g. of rubber. When moisture was present, products richer in O were formed. Absorption of the calcd. amt. of perbenzoic acid was almost complete in a short time. The attempt was made to obtain the "oily form" of rubber described by Harries by letting stand in the warm sunlight for 1 mo. a C₆H₆ soln. of rubber in a brown bottle under a CO₂ atm. By pptg. with EtOH, a product insol. in Et₂O and with the regular properties of rubber was obtained. *Coagulation of rubber in boiling C₆H₆*.—No change was obtained by boiling a 2% rubber soln. in C₆H₆ in the presence of CO₂, but with a 4% soln. a yellowish jelly was deposited on the sides and bottom of the flask. No deposit was formed at 50° after 10 hrs. This gel formation was reversible, for by rapid cooling the gel remaining went into soln. on shaking or on standing at room temp. Analysis of the gel gave (C₈H₈)₂.

C. C. DAVIS

Kirchhof's recent investigations of the constitution of types of rubber. WALTHER HERZOG. *Oester. Chem. Zig.* 25, 157(1922).—The results of Pummerer and Burkard (cf. preceding abstr.) are sufficient evidence to prove that rubber has the empirical formula (C₈H₈)₂ and not C₁₀H₁₇ according to the contention of Kirchhof (cf. C. A. 16, 4363).

C. C. DAVIS

Reclaimed rubber. J. TORREY. *Chem. News* 125, 197-8(1922).—A short description of the relative status and methods of British and American reclaiming.

C. C. DAVIS

Possibilities in rubber latex. J. A. HUNTER. *Textile World* 62, 3014-7(1922).—A very general discussion of the results obtained by expts. in using latex in the manuf. of paper and paper substances for special purposes, cotton sizing, cloth finishing, water-proofing, etc.

CHAS. E. MULLIN

Far-reaching developments with rubber latex. ANON. *India Rubber World* 67, 297-9(1923).—Rubber which shows on vulcanization higher tensile strength and greater resistance to abrasion than rubber prepd. in the usual way can be made by drying atomized latex by means of hot air, atomization being brought about by running the latex on to a rapidly rotating disk at the top of a chamber about 30 ft. in height and in diam. The rubber particles fall on to a conveyor; they form a spongy mass. Compounding ingredients may be mixed with the latex before it is dried. (Cf. U. S. pat. 1,423,525; C. A. 16, 3232). When thread or yarn is immersed in latex, rubber penetrates to the center of the strands and is observable in the hollow tubules of many of the fibers.

After vulcanization, fabric which has been treated with latex shows, when used in tires, better endurance than fabric which has been coated with rubber from soln. Rubber deposited from latex vulcanizes more quickly than that deposited from soln. Latex-treated fabric is prepd. suitably by leading a series of parallel cords from spools on a creel through latex contained in a tank, and then drying the latex fabric so formed on a series of drying cans. (Cf. U. S. pat. 1,424,020; Brit. pat. 178,811; C. A. 16, 3234, 4364.)

G. S. WHITBY

The coagulation of latex. L. LINDBT. *Compt. rend.* 175, 798-9(1922).—With reference to the observation of Vernet (C. A. 17, 481) that the wt. of the coagulum obtained from latex by CaCl_2 is greater than that ordinarily obtained, L. draws attention to his observations (C. A. 7, 3976; 8, 3307; 9, 2113) that, in the case of milk, the effect of CaCl_2 in augmenting the wt. of the coagulum obtained is due to its pptg. from the serum phosphates and citrates which have the ability to hold part of the milk proteins in soln.

G. S. WHITBY

Water dispersions from coagulated rubber, balata, and gutta-percha. I. JOHN B. TURRILL. *India Rubber World* 67, 213-5(1923).—Dispersions of rubber in water have been successfully made, the particles being of approx. the same size as those in rubber latex. The rubber in such dispersions can be coagulated by the addn. of AcOH . (No particulars of the method of prep. such dispersions are given in the present paper.) It is thought possible that such dispersions may be useful in eliminating variation between raw rubber samples. T. advances the hypothesis that the globules, which are considered as being surrounded by a membrane, present in latex still exist in rubber, and that the occurrence of depolymerization and tackiness in rubber depends essentially on the breakdown of the supposed membranes.

G. S. WHITBY

Experiments with rubber, celluloid, and hexalin. FORDYCE JONES. *Rubber Age* 12, 205(1922).—Neither rubber (R) nor celluloid (C) could be dissolved in hexalin (H) (cf. C. A. 15, 908, 1081, 1824, 3912) by shaking for 3 days or by heating to the b. p., though the R swelled somewhat by the latter method. C solns. in amyl acetate and R in benzine, however, were easily miscible, without subsequent sepn., by addn. of 0.2 of the total vol. of H at room temp. When hot the mixt. dried out without sepn. Used as varnish, this mixed soln. adhered well to metals and to glass. Painted on wood, leather, cured rubber, etc., it dried fairly quickly with a high polish, though unsuitable for flexible materials. By varying the % of R and C, clear products of good tensile strength were obtained, but were very slow in drying. The soln. is suggested for use both in the plastic state and for making dipped goods, for even under very unfavorable conditions a high gloss can be obtained. A soln. contg. only 5% C burned easily, and investigation of cellulose acetate as a substitute is recommended.

C. C. DAVIS

The manufacture of golden antimony sulfides. GIRO SILVIO. *Caoutchouc & gutta-percha* 19, 11640-1(1922).—An outline of the chemistry involved in the large-scale manuf. of golden Sb sulfides from quartz Sb minerals, supplemented by a description of the results attainable with these pigments in rubber compds.

C. C. D.

The manufacture of carbon blacks in France in relation to that of rubber. M. OSWALD. *Caoutchouc & gutta-percha* 19, 11641-4(1922).—An outline of the present-day manuf. and uses of C blacks in France and abroad, with a description of the properties imparted to rubber by these materials. On account of the lack of natural gas in France, blacks of equiv. value have been developed by burning naphthalene and anthracene. Besides being based upon an ever-increasing supply of naphthalene, these processes recover 50-5% of the C instead of the 1.5-3.5% yield of gas black from CH_4 .

C. C. DAVIS

Akron's unique course in rubber chemistry. H. E. SIMMONS. *India Rubber Rev.* 22, No. 8, 41-2(1922).—Descriptive.

C. C. DAVIS

Some problems in the manufacture of rubber heels. MORRIS OMANSKY. *Rubber Age* 12, 206-9(1922).—The problems and difficulties of the manufacturer and the consumer of rubber heels are presented from both points of view. C. C. DAVIS

Clay in rubber compounding. E. L. DAVIES. *India Rubber Rev.* 22, No. 10, 22-23, 82(1922).—A general discussion of the merits of ground clays. The hypothesis is offered that the value of a material as filler is a function of its unsatd. or residual adsorbing capacity. Accordingly both the particular material and the shape of the particle are of great influence. Fine, porous or irregular particles have a max. surface and are the most effective reinforcing fillers. With clays, hexamethylenetetramine is said to give the best results of any accelerator. C. C. DAVIS

Zinc oxide in compounds. E. L. DAVIES. *India Rubber Rev.* 22, No. 11, 37-8, 116(1922).—The importance and present adaptability of ZnO as a compounding ingredient are described. C. C. DAVIS

Dithio acids and their derivatives as ultra-accelerators of vulcanization. G. BRUNI. *India-Rubber J.* 64, 937(1922).—Zn dithiobenzoate and Zn dithiopyromucate can, in the presence of ZnO, bring about the vulcanization of a rubber-S mixt. in a few mins. at 144° or in a longer period at room temp. Dithiobenzoyl disulfide is capable, in the presence of ZnO, of bringing about vulcanization without additional S (cf. C. A. 16, 1887). Salts of dithioacids can be prepd. by the action of an aq. soln. of an inorg. (especially ammonium) polysulfides upon an aldehyde; positive results being obtained with benzaldehyde, salicylaldehyde, anisaldehyde, and furfural. Aliphatic aldehydes, e. g., MeCHO, citral, and citronellal, also react with NH_4 polysulfide. (Cf. succeeding abst.) G. S. WHITBY

The action in the vulcanization of rubber of homo- and hetero-cyclic dithio acids and their derivatives, and of nitrogen sulfide. E. ROMANI. *Caoutchouc & gutta-percha* 19, 11626-9(1922).—In a mixt. of 100 rubber, 2 S, and 2 ZnO, 2 pts. dithiobenzoic acid (A) leads to vulcanization in 5 mins. at a pressure of about 3 atms. or in 2 days at ordinary temp. The Zn salt of A shows similar accelerating properties; the Pb salt is less active. Dithiobenzoyl disulfide is an auto-ultra-accelerator, 5 pts. bringing about the vulcanization of a mixt. of 100 rubber and 5 ZnO in 15 mins. at 3 atms. or in 45 mins. at 80°. Dithiopyromucic acid (B) and its corresponding derivs. act similarly to but more powerfully than A and its above mentioned derivs. Monothiobenzoic acid, its Zn salt, and disulfide are quite inactive as accelerators of vulcanization. Similarly, in contrast to Zn Et xanthate and dixanthogen, $\text{Zn}(\text{S.CO.OEt})_2$ and $(\text{EtO.CO.S})_2$ are without accelerating action. The best method available for the prepn. of dithio acids is a modification of the method of White (C. A. 9, 613); an aldehyde in alc. soln. is treated with NH_4 polysulfide. In addition to A, the following were prepd. by this method: dithio-salicylic, -anisic, -pyromucic (from furfural), -vanillic, and -piperonylic acids. (Of these the last three have not been prepd. hitherto, and will shortly be described in full.) The Zn salts and disulfides were prepd. in all cases. In vulcanization all these substances behave like A or its corresponding deriv. Furfuramide (C), when heated in alc. soln. with S and H_2S , yields B. In an atm. of H_2S at 100° C will bring about the vulcanization of a mixt. of rubber, ZnO, and S in a comparatively short time. Hence it is believed that the accelerating action of benzamide (hydrobenzamide. ABSTR.), C, and similar compds. is due to the following succession of reactions: (a) decompn. into aldehyde and NH_4 , (b) reaction of the NH_4 with H_2S (formed during vulcanization) to yield NH_4 polysulfide, (c) action of the latter on the aldehyde to yield a dithio acid, (d) oxidation of the latter to the disulfide, (e) liberation of S available for vulcanization, followed by union with further S, and so on (Cf. Bruni and Romani, C. A. 15, 3915). Suitable methods of incorporating ultra-accelerators in rubber mixts. are discussed. N_2S_4 is both an ultra-accelerator and an auto-ultra-

accelerator; 2 pts. will bring about the vulcanization of 100 pts. of rubber in 5 min. at 2' atm. ZnO is without effect on its action.

G. S. WHITBY

TUTTLE, JOHN B. **The Analysis of Rubber.** New York: The Chemical Catalog Company. 158 pp. \$2.50. Reviewed in *J. Franklin Inst.* **194**, 847(1922).

Rubber composition. A. BIDDLE. U. S. 1,437,487, Dec. 5. A compn. adapted for tires, mats, billiard balls or other articles is formed of rubber latex etc. and casein together with S and fillers or modifying ingredients such as are commonly used in rubber mixts.

Rubber composition. R. R. WILLIAMS. U. S. 1,438,735, Dec. 12. The particles of fillers for use with rubber are coated with an adhesive material such as a rubber soln. for binding the particles firmly to the rubber.

Rubber and ebonite substitute. H. PLAUSON. Can. 226,632, Nov. 28, 1922. An unsatd. org. acid, a vulcanizable oil and S are heated to produce the desired product.

Chicle substitute for chewing gums. L. W. BUCKLEY. U. S. 1,438,019, Dec. 5. Pontianac gum is treated with a mildly alk. soln. of Na_2PO_4 and a small amt. of Na diborate to emulsify oily matter and neutralize acids and the gum thus treated is washed with hot H_2O to render it suitable for use as a chewing-gum base.

Deflocculating clay. W. FELDENHEIMER. U. S. 1,438,587, Dec. 12. Clay is suspended in H_2O with Na_2CO_3 , NH_3 or other deflocculating agent and the suspension is evapd. to dryness to obtain a product suitable for use in *rubber mixts.* U. S. 1,438,588 specifies the use of Na pyrophosphate or metaphosphate or the free acids for deflocculating clay in dil. aq. mixt. Na_2CO_3 also may be used. Cf. *C. A.* **17**, 194.

